mism concerning the generality of linear free energy relations was premature. Of course such correlations are helpful in understanding some of the grosser features of patterns of reactivity.

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Dissociation Kinetics of Metal Ion–2,6-Dicarboxypiperidineacetic Acid Complexes: Nickel(II) and Cadmium(II)

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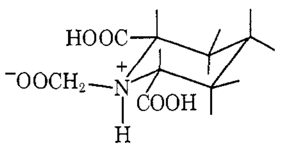
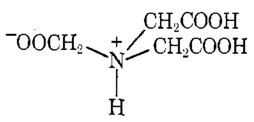
The kinetics of the dissociation of the nickel(II) and cadmium(II) complexes of 2,6-dicarboxypiperidineacetic acid (DPA) have been measured. For the NiDPA dissociation, the results are consistent with the rate law $-d[\mathrm{NiDPA}]/dt = (k_{\mathrm{Cu}}{}^{\mathrm{NiDPA}} \cdot [\mathrm{Cu}^{2+}] + k_{\mathrm{H}}{}^{\mathrm{NiDPA}}[\mathrm{H}^+] + k_{\mathrm{H}^2}{}^{\mathrm{NiDPA}}[\mathrm{H}^+]^2)[\mathrm{NiDPA}]$. The values of the rate constants at 25.0 ± 0.1° and the activation energies are, respectively: $(3.0 \pm 0.3) \times 10^{-3}\ M^{-1}\ \mathrm{sec}^{-1}$, 12.2 ± 1 kcal mol^{-1}; $(8.0 \pm 0.2) \times 10^{-1}\ M^{-1}\ \mathrm{sec}^{-1}$, 14.3 ± 1 kcal mol^{-1}; $(2.95 \pm 0.09) \times 10^{2}\ M^{-2}\ \mathrm{sec}^{-1}$, 12.1 ± 0.5 kcal mol^{-1}. For the CdDPA dissociation, the rate law is $-d[\mathrm{CdDPA}]/dt = (k^{\mathrm{CdDPA}} + k_{\mathrm{H}}{}^{\mathrm{CdDPA}}[\mathrm{H}^+] + k_{\mathrm{H}^2}{}^{\mathrm{CdDPA}}[\mathrm{H}^+]^2)[\mathrm{CdDPA}]$. The values of the rate constants at 25.0 ± 0.1° are $4.9 \pm 0.4\ \mathrm{sec}^{-1}$, $(3.3 \pm 0.3) \times 10^{5}\ M^{-1}\ \mathrm{sec}^{-1}$, and $(5.1 \pm 0.2) \times 10^{9}\ M^{-2}\ \mathrm{sec}^{-1}$, respectively.

Introduction

Recently the preparation and metal ion stability constants of 2,6-dicarboxypiperidineacetic acid (DPA) have been reported.[1] The ligand possesses the same bonding groups as nitrilotriacetic acid, but the nitrogen and the α carbons of two of the three acetate groups form part of a six-membered saturated ring. Nmr data[1b] indicate that the three substituents on the ring are all in equatorial positions as shown. Models suggest that the ring holds these two acetate groups in close proximity to the central metal ion and therefore the dissociation of the metal complex may be hindered.



DPA



NTA

The present study investigates the effect of the ring structure on the dissociation reactions of the nickel(II) and cadmium(II) complexes. The rates of dissociation of these complexes can be compared to the rates of dissociation of the nitrilotriacetate (NTA) complexes, which have previously been measured. In the case of nitrilotriacetatonickelate(II)[2] and other nickel systems,[3,4] the reaction has been postulated to proceed through dinuclear intermediates with the breaking of the nickel–nitrogen bond being the rate-determining step. Studies of the nitrilotriacetatocadmate(II)[5] dissociation suggest that the reaction pathways are similar to those observed with nitrilotriacetatonickelate(II), but the rate-determining step has not been elucidated.

The dissociation of the nickel(II) complex was followed by conventional spectrophotometry, measuring the exchange with copper(II). The data are consistent with the chemical system

$$\mathrm{NiDPA^- + Cu^{2+}} \xrightarrow{k_{\mathrm{Cu}}{}^{\mathrm{NiDPA}}} \mathrm{CuDPA^- + Ni^{2+}} \qquad (1)$$

$$\mathrm{NiDPA^- + H^+} \xrightarrow{k_{\mathrm{H}}{}^{\mathrm{NiDPA}}} \mathrm{Ni^{2+} + HDPA^{2-}} \qquad (2)$$

$$\mathrm{NiDPA^- + 2H^+} \xrightarrow{k_{\mathrm{H}^2}{}^{\mathrm{NiDPA}}} \mathrm{Ni^{2+} + H_2DPA^-} \qquad (3)$$

$$\mathrm{Cu^{2+}} + \begin{bmatrix}\mathrm{HDPA^{2-}}\\ \mathrm{H_2DPA^-}\end{bmatrix} \xrightarrow{\text{rapid}} \mathrm{CuDPA^-} + \begin{bmatrix}\mathrm{H^+}\\ \mathrm{2H^+}\end{bmatrix} \qquad (4)$$

The dissociation of the cadmium(II) complex is much faster and was followed by the analysis of the kinetic wave observed in conventional polarography. The data can be expressed by the equations

$$\mathrm{CdDPA^-} \xrightarrow{k^{\mathrm{CdDPA}}} \mathrm{Cd^{2+} + DPA^{3-}} \qquad (5)$$

$$\mathrm{CdDPA^- + H^+} \xrightarrow{k_{\mathrm{H}}{}^{\mathrm{CdDPA}}} \mathrm{Cd^{2+} + HDPA^{2-}} \qquad (6)$$

$$\mathrm{CdDPA^- + 2H^+} \xrightarrow{k_{\mathrm{H}^2}{}^{\mathrm{CdDPA}}} \mathrm{Cd^{2+} + H_2DPA^-} \qquad (7)$$

$$\begin{array}{c} \underbrace{\mathrm{Cd^{2+} \rightleftharpoons CdOAc^+}} \\ \big\downarrow {+2e} \\ \mathrm{Cd(amal)} \end{array} \qquad (8)$$

In acetate media, free Cd^{2+} (produced in eq 5–7) and cadmium acetate complexes are in rapid equilibrium and these species undergo rapid electrochemical reac-

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tion (eq 8) at a dropping mercury electrode to produce cadmium amalgam.

Experimental Section

2,6-Dicarboxypiperidineacetic acid was prepared by the reaction of chloroacetic acid with piperidine-2,6-dicarboxylic acid using the method of Kundra and Thompson.[1] Solutions of 2,6-dicarboxypiperidineacetic acid were standardized by direct titration (using murexide indicator) against a primary standard copper nitrate solution and by acid–base titration using a glass indicator electrode. Results of these titrations agreed to within 0.3% of the theoretical value. Nickel perchlorate, copper perchlorate, and cadmium nitrate solutions were standardized by EDTA titration. Solutions of NiDPA and CuDPA were prepared from equimolar quantities of the metal perchlorate and DPA solutions, followed by pH adjustment to 4.5.

In the NiDPA study, the experimental procedures were similar to those previously reported.[2] The ionic strength was maintained at 1.25 *M* with sodium perchlorate. No buffer was used. The reactions were followed spectrophotometrically using 5-cm cells at the 675-nm absorption band of CuDPA. The values of $\epsilon_{\mathrm{NiDPA}}$, ϵ_{Ni}, ϵ_{Cu}, and $\epsilon_{\mathrm{CuDPA}}$ are 3.9, 1.8, 4.4, and 39.0 M^{-1} cm^{-1}, respectively. The values of $\epsilon_{\mathrm{NiDPA}}$ and $\epsilon_{\mathrm{CuDPA}}$ are independent of pH in the range 2.7–4.5, indicating no evidence for any acid species such as HNiDPA.

An isosbestic point is observed when a repetitive spectral scan is made during the reaction of equimolar concentrations of reactants, thus indicating a transition from a set of reactants in rapid equilibrium to a similar set of products without any buildup of intermediates. An infinite-time spectrum is compatible with the assignment of CuDPA and nickel(II) as products.

All rate solutions contained excess Ni(II) to repress prior dissociation of NiDPA. The concentration of Ni(II) in excess had no effect on the rate. The Cu^{2+} concentration was in large excess and constant during the rate run. The back-reaction was negligible under the conditions used. The rate can be expressed as

$$\frac{-\mathrm{d}[\mathrm{NiDPA}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{CuDPA}]}{\mathrm{d}t} = k_{\mathrm{o}}[\mathrm{NiDPA}] \qquad (9)$$

where k_{o} is the total observed first-order rate constant. Values of k_{o} were obtained from typical straight-line plots of log $(A_\infty - A_t)$ *vs.* time, where A_∞ and A_t are the absorbance values at infinite time and at time *t*, respectively. The reactions were followed for at least 70% conversion to CuDPA and were reproducible to ±5%.

In the CdDPA study, all reaction solutions were maintained at an ionic strength of 0.20 *M* with $NaNO_3$. The solutions were buffered with acetic acid and sodium acetate. The sodium acetate concentration was maintained at 0.05 *M* and the acetic acid concentration was varied from 0.025 to 0.175 *M*. The pH was measured with a Corning Model 12 expanded-scale pH meter. DPA was present in excess and in the pH range studied, 4.0–5.1, exists primarily as the monoprotonated species HDPA.

All solutions to be measured polarographically were degassed with purified nitrogen for 20 min prior to measurement. A nitrogen atmosphere was maintained above the solution during measurement. The nitrogen used was first passed through an oxygen scrubbing tower, a dilute base tower, and an acetic acid–sodium acetate tower before passing through the solution of interest.

Polarographic waves were recorded from −0.500 to −1.000 V *vs.* a saturated calomel electrode using a Beckman Electroscan 30. The scanning speed was 0.060 V/min and damping was 0.5 sec. All polarographic waves were recorded in triplicate at each of three drop times. Drop times were measured in duplicate at the half-wave potential of the kinetic wave.

In the polarographic scan, two waves are observed. The first, a kinetic wave, is due to the reduction of cadmium(II), aqueous ions, and acetate complexes, formed upon dissociation of the CdDPA complex during the lifetime of the mercury drop. The second, a diffusion wave, is due to the reduction of the CdDPA complex. The two waves are not completely separated, and kinetic currents, i_{k}, and diffusion currents, i_{d}, were obtained using the method given by Meites.[6]

Table I

NiDPA–Cu(II) Reaction. Observed First-Order Rate Constants at 25.0°, μ = 1.25, [NiDPA] = 3.03 × 10^{-3} *M*, $[Cu^{2+}]$ = 3.03 × 10^{-2} *M*, and $[Ni^{2+}]$ = 2.80 × 10^{-3} *M*

$10^4[H^+]$, *M*	10^4k_o, sec^{-1}	10^4k_o (calcd), sec^{-1}	$10^4[H^+]$, *M*	10^4k_o, sec^{-1}	10^4k_o, (calcd), sec^{-1}
1.04	1.86	1.83	13.5	16.6	17.2
1.17	1.99	1.94	14.1	18.6	18.1
2.07	2.83	2.75	14.4	18.5	18.6
2.40	3.07	3.06	14.7	19.0	19.1
3.39	3.93	4.02	16.4	22.1	22.0
5.16	5.92	5.89	16.4	22.8	22.0
5.88	6.82	6.70	17.5	24.3	24.0
6.53	7.48	7.46	18.0	25.0	25.0
7.41	8.09	8.52	18.5	26.3	25.9
8.15	9.43	9.46	19.5	28.0	27.8
9.55	11.8	11.3	20.2	29.3	29.2
9.98	12.0	11.9	20.2	29.8	29.2
10.6	12.4	12.8	21.3	31.3	31.4
12.5	15.5	15.6	23.6	35.7	36.3
13.3	17.2	16.8	25.6	40.0	40.8

The rate constants were evaluated from the values of i_{k} and i_{d} using the treatment employed by Koryta[5] in the polarographic study of the CdNTA dissociation. Under the conditions used, the following equation used by Koryta applies

$$\frac{i_{\mathrm{k}}}{i_{\mathrm{d}} - i_{\mathrm{k}}} = 0.886\sqrt{\frac{k(1 + K_1[\mathrm{OAc}^-] + K_1K_2[\mathrm{OAc}^-]^2 + \ldots)[\mathrm{H}^+]t}{K_{\mathrm{CdDPA}}K_{\mathrm{a3}}C}} \qquad (10)$$

Where *k* is the over-all rate constant for the dissociation of the complex, *C* is the total concentration of free ligand, and *t* is the drop time of the dropping mercury electrode. Values[1] of the stability constant (K_{CdDPA}) for CdDPA and the third acid dissociation constant (K_{a3}) for the ligand are $10^{+8.81}$ and $10^{-9.33}$, respectively. The terms in the sum $(1 + K_1[\mathrm{OAc}^-] + K_1K_2 \cdot [\mathrm{OAc}^-]^2 + \ldots)$ express the relative amounts of aqueous cadmium ions and acetate cadmium complexes. K_1 and K_2 are the successive stability constants of the acetate complexes and $[\mathrm{OAc}^-]$ is the acetate concentration.

The sum was evaluated[7] by measuring the change in $E_{1/2}$ of the Cd^{2+} polarographic wave as the acetate concentration was varied in the absence of DPA. At the acetate concentration (0.05 *M*) used in the rate studies, a value of 2.15 was obtained for the sum compared to a value of 2.0 obtained by Koryta.[5]

Results

Kinetics of the NiDPA–Cu(II) Reaction.—Table I gives the values of the observed first-order rate constant (k_{o}, eq 9) as $[H^+]$ is varied from 1 to 25 × 10^{-4} *M* at the given concentrations of NiDPA, Ni^{2+}, and Cu^{2+}. These values of k_{o} *vs.* $[H^+]$ can be expressed by

$$k_{\mathrm{o}} = k_1 + k_{\mathrm{H}}^{\mathrm{NiDPA}}[\mathrm{H}^+] + k_{\mathrm{H}^2}^{\mathrm{NiDPA}}[\mathrm{H}^+]^2 \qquad (11)$$

The individual rate constants can be graphically resolved and have values of 9.6 × 10^{-5} sec^{-1}, 8.0 × 10^{-1} M^{-1} sec^{-1}, and 2.95 × 10^2 M^{-2} sec^{-1}, respectively. Table I also gives the value of k_{o} calculated using the above values. The agreement is well within the experimental error.

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TABLE II

NiDPA–Cu(II) REACTION. VARIATION OF NiDPA AND Ni^{2+} AT 25.0°, $\mu = 1.25$, AND $[Cu^{2+}] = 3.03 \times 10^{-2}$ M

No.	10^3 [NiDPA], M	$10^3[Ni^{2+}]$, M	$10^4[H^+]$, M	10^4k_o, sec^{-1}	10^4k_o (calcd), sec^{-1}
1	1.01	2.80	8.77	9.58	10.3
2	1.01	2.80	20.00	28.2	28.8
3	2.02	2.80	9.00	10.2	10.5
4	2.02	2.80	19.90	29.2	28.6
5	3.03	2.80	19.50	28.0	27.8
6	3.03	1.87	20.10	29.0	29.0
7	3.03	0.93	20.00	28.3	28.8

TABLE III

NiDPA–Cu(II) REACTION. VARIATION OF OBSERVED RATE CONSTANT WITH Cu^{2+} AT 25.0°, $\mu = 1.25$, [NiDPA] $= 3.03 \times 10^{-3}$ M, AND $[Ni^{2+}] = 2.80 \times 10^{-3}$ M

No.	10^2 $[Cu^{2+}]$, M	$10^4[H^+]$, M	10^4k_o, sec^{-1}	$10^4(k_o - H^+$ terms), sec^{-1}	$10^3k_{Cu}^{NiPDA}$, M^{-1} sec^{-1}
1	1.01	1.240	1.34	0.30	3.0
2	2.02	2.000	2.29	0.57	2.8
3	3.03	...	...	0.96[a]	3.2
				Av	3.0

[a] Value of intercept, data of Table I.

Table II gives the values of k_o as the NiDPA (no. 1–5) and excess Ni^{2+} (no. 5–7) concentrations are varied. The agreement between the observed values of k_o and the values calculated using eq 11 and the constants given above clearly shows that the rate is independent of Ni^{2+} and first order in NiDPA.

The $[Cu^{2+}]$ dependence of k_o at low H^+ concentrations is given in Table III. The values of k_o can be corrected for their hydrogen ion contribution by subtracting out the value of $k_H^{NiDPA}[H^+] + k_{H_2}^{NiDPA} \cdot [H^+]^2$. Thus, the value of k_1 is $[Cu^{2+}]$ dependent and the value of k_{Cu}^{NiDPA} equal to $k_1/[Cu^{2+}]$ is given in Table III. As the hydrogen ion concentration is increased, the k_1 term contributes less to the observed value of k_o and the copper(II) dependence tends to vanish. This implies that there are no terms that depend on both Cu^{2+} and H^+ concentrations simultaneously. The final expression for the rate is

$$\frac{-d[\mathrm{NiDPA}]}{dt} = (k_{Cu}^{NiDPA}[Cu^{2+}] + k_H^{NiDPA}[H^+] + k_{H^2}^{NiDPA}[H^+]^2)[\mathrm{NiDPA}] \quad (12)$$

The error in the values of k_H^{NiDPA} and $k_{H_2}^{NiDPA}$ is ±3% and for the value of k_{Cu}^{NiDPA} it is ±10%. These errors also hold for the constants measured at the other temperatures.

The temperature dependence of all three reaction paths was studied between 15.0 and 35.0° at an ionic strength of 1.25 M $NaClO_4$ by means of similar sets of experiments at these two temperatures. The results follow the Arrhenius expression and the kinetic parameters for the three constants are given in Table IV.

Kinetics of the CdDPA Dissociation.—As a test of eq 10, the product of $C^{1/2}i_k/(i_d - i_k)$ should be a constant as the excess ligand concentration is varied while the other terms are held constant. Table V shows the constancy of this value. Agreement is well within experimental error.

TABLE IV

NiDPA–Cu(II) REACTION

Variation of Rate Constants with Temperature

Temp, °C	$10^3k_{Cu}^{NiDPA}$, M^{-1} sec^{-1}	$10k_H^{NiDPA}$, M^{-1} sec^{-1}	$10^{-2}k_{H^2}^{NiDPA}$, M^{-2} sec^{-1}
15.0	1.8	3.20	1.50
25.0	3.0	8.02	2.95
35.0	6.2	15.5	5.75

Kinetic Parameters

Rate constant	E_a, kcal/mol	$\Delta S^{\neq}$, eu	$10^{-9}A$
k_{Cu}^{NiDPA}	12.2	−31	0.0025
k_H^{NiDPA}	14.3	−13	22
$k_{H^2}^{NiDPA}$	12.1	− 8.7	200

TABLE V

CdDPA DISSOCIATION. VARIATION OF $i_k/(i_d - i_k)$ WITH LIGAND CONCENTRATION AT $[Cd(II)] = 9.52 \times 10^{-5}$ M, [ACETATE] $= 0.050$ M, AND $[H^+] = 2.91 \times 10^{-5}$ M

Ligand concn, C	$i_k/(i_d - i_k)$	$C^{1/2}i_k/(i_d - i_k)$	Ligand concn, C	$i_k/(i_d - i_k)$	$C^{1/2}i_k/(i_d - i_k)$
Drop Time 3.70			Drop Time = 4.60 sec		
0.010	1.05	1.05	0.010	1.23	1.23
0.020	0.77	1.09	0.020	0.87	1.23
0.025	0.66	1.06	0.025	0.76	1.20
0.030	0.62	1.07	0.030	0.69	1.19
0.040	0.50	1.00	0.040	0.59	1.18

TABLE VI

CdDPA DISSOCIATION. VARIATION OF k WITH HYDROGEN ION CONCENTRATION AT $[Cd(II)] = 9.52 \times 10^{-5}$ M, [DPA] $= 0.025$ M, AND [ACETATE] $= 0.050$ M

$10^5[H^+]$, M	k, sec^{-1}	Std dev, sec^{-1}	k (calcd), sec^{-1}
0.735	7.3	0.8	7.6
1.42	10.6	0.8	10.6
2.19	15.9	1.5	14.5
2.91	19.2	0.9	18.8
2.91	18.9[a]	1.6	18.8
3.66	21.1	2.3	23.7
5.46	36.2	1.7	38.0
6.24	48.1	3.8	45.2
7.35	53.2	4.1	56.5
7.98	66.1	2.9	63.5

[a] Average of values from data in Table V.

Table VI gives the values of k obtained as the $[H^+]$ is varied at a constant ligand concentration of 0.025 M. The results are averages of three trials at three different drop times. The value of k itself is a function of $[H^+]$ and was resolved by the method of weighted least squares to fit the equation

$$k = k^{CdDPA} + k_H^{CdDPA}[H^+] + k_{H^2}^{CdDPA}[H^+]^2 \quad (13)$$

The weight given to each point was $1/S^2$ where S is the standard deviation in Table VI. The values of k^{CdDPA}, k_H^{CdDPA}, and $k_{H_2}^{CdDPA}$ are 4.9 sec^{-1}, 3.3×10^5 $M^{-1}sec^{-1}$, and 5.1×10^9 M^{-2} sec^{-1}, respectively. The last column in the table gives the calculated value of k using the above values. The error in the values of k^{CdDPA} and k_H^{CdDPA} is ±10% and for $k_{H_2}^{CdPDA}$ it is ±5%. The final expression for the rate of dissociation of CdDPA can then be expressed as

$$\frac{-d[\mathrm{CdDPA}]}{dt} = (k^{CdDPA} + k_H^{CdDPA}[H^+] + k_{H^2}^{CdDPA}[H^+]^2)[\mathrm{CdDPA}] \quad (14)$$

Discussion

The dissociation of NiDPA proceeds through reaction pathways similar to those observed with NiNTA.[2,8] Both systems include terms for Cu^{2+} and H^+ attack—rate constants k_{Cu}^{NiDPA}, k_{Cu}^{NiNTA} and k_H^{NiDPA}, k_H^{NiNTA}, respectively. Some minor differences are observed. The simple dissociation path (k^{NiNTA}) of NiNTA is not observed with NiDPA and the NiDPA system shows a squared H^+-dependent term ($k_{H^2}^{NiDPA}$) that is not observed in the NiNTA system. The NiDPA system was studied at somewhat higher acidities and this can account for these differences.

The rate constants for the two systems are of the same order of magnitude and initially suggest that steric factors are small. Considering the H^+ and Cu^{2+} paths for the two systems, the ratios k_H^{NiNTA}/k_H^{NiDPA} and $k_{Cu}^{NiNTA}/k_{Cu}^{NiDPA}$ can be predicted in a manner analogous to the comparison made between the NiNTA and NiEDTA systems.[2] In this comparison, it must be assumed that the same rate-determining step is involved and that steric hindrance is not important. The predicted values of k_H^{NiNTA}/k_H^{NiDPA} and of $k_{Cu}^{NiNTA}/k_{Cu}^{NiDPA}$ are identical, 0.41, and reflect the difference in the stability constants[1,9] of NiNTA ($10^{11.26}$) and NiDPA ($10^{10.87}$). Any statistical effects are not included in the predicted value. The observed ratios are 0.54 and 0.46, respectively. The agreement is good but probably fortuitous when the energy and entropy of activation are considered. The values of E_a for the NiNTA system are approximately 18 kcal/mol for all paths, whereas they are considerably lower (12–14 kcal/mol) for the NiDPA system. This suggests a weaker nickel–nitrogen bond in the nickel complex, as a result of strain due to the ring structure in the ligand. However, this lower energy of activation is offset by the entropies of activation, which are more negative in the NiDPA system. The values of $\Delta S^{\ddagger}$ associated with k_H^{NiNTA} and k_{Cu}^{NiNTA} are −1 and −13 eu compared to −13 and −31 eu for the similar NiDPA paths. The large changes in $\Delta S^{\ddagger}$ suggest that ring orientation has a significant effect on the formation of the intermediates. Similarly the values of the frequency factor, A, are much lower for the NiDPA pathways.

No attempt was made to determine E_a, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ for the CdDPA system since the experimental method employed gives rate constants good to only ±10% and leads to large errors in these values. Even though the cadmium(II) reactions are approximately five orders of magnitude faster than the nickel(II) reactions, similarities suggest that the reactions proceed through closely related intermediates. The ratio[10] k_H^{CdDPA}/k^{CdDPA} (6.7×10^4) is in agreement with similar ratios for CdNTA and NiNTA, 1.9×10^5 and 1.2×10^5, respectively. Like the NiNTA and NiDPA systems, the ratio k_H^{CdNTA}/k_H^{CdDPA} (0.9) reflects the difference in stability constants[1,9] of CdNTA ($10^{9.80}$) and CdDPA ($10^{8.81}$). It is therefore not unreasonable to assume that the ring structure in the DPA ligand shows similar effects in the dissociation of the cadmium(II) complex, lowering the energy of activation and the frequency factor.

Acknowledgment.—This work was supported by the National Science Foundation, Grant GP-7319.

[8] Values[2] of k_{Cu}^{NiNTA}, k_H^{NiNTA}, and k^{NiNTA} are 1.39×10^{-3} M^{-1} sec^{-1}, 4.34×10^{-1} M^{-1} sec^{-1}, and 3.5×10^{-6} sec^{-1}, respectively.

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[10] Values of k^{CdNTA} (1.6 sec^{-1}) and k_H^{CdNTA} (3.0×10^6 M^{-1} sec^{-1}) are taken from ref 5.

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Spectroscopic Studies of Some Carbene Pentacarbonyl Complexes of Chromium(0) and Tungsten(0)

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Infrared, nuclear magnetic resonance, and electronic spectral studies of several $M(CO)_5C(OC_2H_5)R$ compounds have been carried out, where M = Cr and W and R = CH_3, n-C_4H_9, and C_6H_5. σ- and π-bonding properties of the carbene ligands are interpreted using Graham's approach. These results indicate the carbene ligands to be comparable to phosphines in σ-donor strengths and much better σ donors than a carbonyl ligand. At the same time the carbene groups behave as strong π acceptors.

Introduction

The reaction of organolithium compounds with carbon monoxide and with metal carbonyls has been reported as a new method for synthesis of ketones and aldehydes.[2] The discovery that alkylation of lithium salts of the organolithium–metal carbonyl addition product leads to a carbene-type ligand (eq 1) has raised considerable interest in organometallic chemistry.[3]

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