solvation of methylamine than ammonia. The heat of hydration of gaseous methylamine is −11.2 kcal. mole^{-1} compared to −8.3 kcal. mole^{-1} for ammonia. Enthalpy differences of this order of magnitude have an appreciable effect on the stability constants and must play an important role in affecting the instability of the alkylamine complexes. One might also expect that another factor contributing to the stability difference is the larger solvation of the ammonia complex than the alkylamine complexes. The spectrochemical data indicate the instability is not attributed to the relative strength of the metal ion–ligand interaction of water and the alkylamines.

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Notes

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Polarographic Determination of the Cadmium Complexes of Pyrazole[1]

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Pyrazole (1,2-diazole), like its isomer imidazole, is a monodentate ligand. Furthermore, pyrazole is an extremely weak Lewis base ($pK_a = 2.53$ at 25°) and would not be expected to form strong coordination compounds. This could explain the absence of pyrazole complex data in the literature. The complex-forming tendency of pyrazole with cadmium(II) has been investigated. It was of interest to determine the stability of the complexes and to determine the extent of reaction as indicated by the highest ordered complex formed. In addition to the stability constants and stoichiometry of the complexes, it was desirable to evaluate the enthalpy changes associated with the complex formation reaction. Accordingly, the investigations described herein were conducted at three temperatures, namely, 0, 25, and 45°. In view of the excellent characteristics of cadmium(II) at the dropping mercury electrode (d.m.e.), the polarographic method was used throughout this investigation.

Experimental

Reagent grade cadmium nitrate and potassium nitrate were used without further purification. Stock solutions of cadmium nitrate were analyzed gravimetrically by conversion to cadmium sulfate. Pyrazole was obtained from K & K Laboratories and the stock solutions were freshly prepared before each investigation.

Polarographic current–voltage curves were obtained with a Sargent Model XXI polarograph. Potential measurements were made *vs.* a saturated calomel electrode (s.c.e.), using a saturated potassium nitrate salt bridge, by means of a Rubicon potentiometer, No. 2730. A Leeds and Northrup pH meter, No. 7663AL, was used for pH measurements. A No. 1199–30 glass electrode was used at 25 and 45°, while measurements at 0° were obtained with electrode No. 1194–44.

All solutions to be analyzed were made up to 5×10^{-4} *M* in cadmium nitrate and 0.1 *M* in potassium nitrate. The concentration of pyrazole varied from 0.05 to 2.0 *M*. Cylinder nitrogen, purified of any traces of oxygen by an alkaline pyrogallol train, was used to remove oxygen from the cell solution. During electrolysis a nitrogen atmosphere was maintained over the solution. Maximum suppressors were not necessary since none of the pyrazole complexes produced maxima.

A constant and reproducible mercury drop time was obtained by means of a capillary standtube affixed to a centimeter scale. In 0.1 *M* potassium nitrate at 25° and at an applied potential of −1.000 volt the capillary characteristics were: $m = 2.44$ mg. sec.$^{-1}$ and $m^{2/3}t^{1/6} = 2.28$ mg.$^{2/3}$ sec.$^{-1/2}$.

Results and Discussion

The proof of reversibility of the electrode reactions and the determination of half-wave potentials was accomplished in the conventional manner as described by Lingane.[3]

The number of pyrazole ligands coordinated to a central cadmium(II) ion was calculated from the slope of plots of $E_{1/2}$ *vs.* the logarithm of the pyrazole concentration according to the equation[3,4]

$$\Delta E_{1/2}/\Delta \log [\text{Py}] = -p(2.303RT)/nF \qquad (1)$$

where p is the number of ligands coordinated.

The stability constants were calculated by application of the relation

$$(E_{1/2})_c - (E_{1/2})_s = -(2.303RT/nF) \log (K_{st} f_s k_c / f_c k_s) - p(2.303RT/nF) \log [\text{Py}] \qquad (2)$$

which is a modification of the usual form[3] for the purpose of placing emphasis upon the stability constant (formation constant) rather than the dissociation constant. In eq. 2, f is the activity coefficient and k is a constant which is proportional to the square root of the diffusion coefficient of the ion. The subscripts c and s refer to the complex and simple ions, respectively. The ratio $f_s k_c / f_c k_s$ is often assumed to be unity. However, in this investigation, at constant ionic strength, only the activity coefficient ratio was assumed to be unity. The ratio k_c/k_s was determined experimentally from the ratio of the observed diffusion cur-

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[1] This investigation was carried out during the tenure of Predoctoral Fellowship No. GF-10,095, United States Public Health Service.

[2] Abstracted in part from the Ph.D. dissertation of J. K. Romary, Kansas State University, 1961.

[3] J. J. Lingane, *Chem. Rev.*, **29**, 1 (1941).

[4] N. C. Li and M. Chen, *J. Am. Chem. Soc.*, **80**, 5678 (1958).

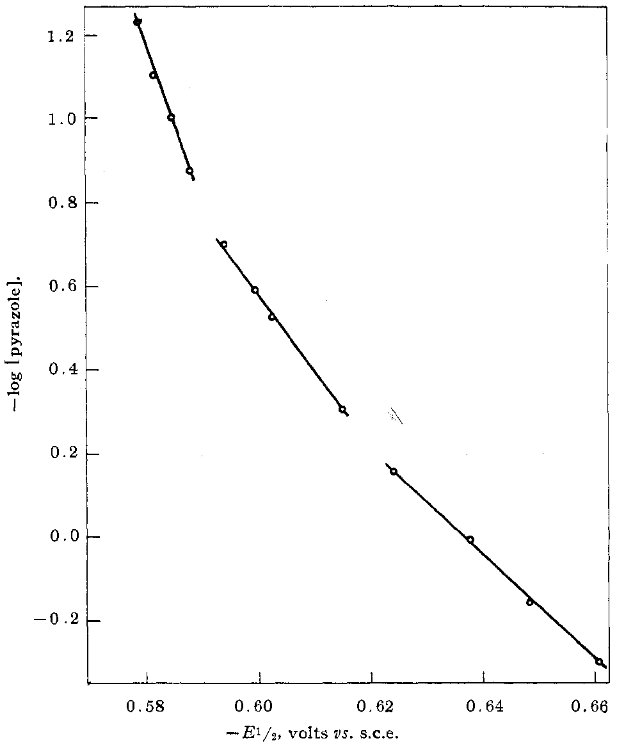

Fig. 1.—Half-wave potential shift for cadmium(II) complexes of pyrazole *vs.* log of pyrazole concentration.

rents of the complex and simple metal ions shown by

$$(i_d)_c/(i_d)_s = (D_c/D_s)^{1/2} = k_c/k_s \qquad (3)$$

which is obtained from the ratio of the Ilkovic equation[5] for the complex and simple metal ions. As a complex ion becomes increasingly bulky its rate of diffusion decreases. The k_c/k_s ratios for $CdPy^{++}$, $CdPy_2^{++}$, and $CdPy_3^{++}$ at 25° are 1.0, 0.94, and 0.83, respectively. A half-wave potential of −0.571 volt was observed for simple cadmium ion at 25° in the system described for this investigation.

The results obtained at 25° are typical of those obtained at all temperatures and are presented in Table I and Fig. 1. It is observed that the plot of $E_{1/2}$ *vs.* log [Py] is composed of three straight lines. The 1:1 complex of cadmium(II) with pyrazole predominates up to a pyrazole concentration of 0.13 *M*. Between 0.20 and 0.50 *M* the predominant species is the 1:2 complex. The highest ordered complex found, namely 1:3, exists above 0.70 *M*. The experimental values of *p* in these three areas are 0.94, 1.8, and 2.8, respectively. Similar results were found at 0 and 45° and are summarized in Table II. Included in Table II are the thermodynamic quantities, $\Delta G°$ and $\Delta H°$, which were derived from the logarithms of the stability constants in the usual manner.

Cadmium(II) usually presents a coordination number of four for monodentate groups and as high as six for polydentate groups.[6] Since pyrazole is monodentate, one might logically expect that the highest ordered complex would be 1:4. However, in view of the low basic strength of the ligand it would seem reasonable that the steric resistance to the addition of a fourth pyrazole molecule could not be overcome. Pyrazole concentrations as high as 2.0 *M* produced no evidence of a 1:4 complex.

TABLE I
POLAROGRAPHIC RESULTS AT 25° FOR SOLUTIONS CONTAINING 5×10^{-4} *M* $Cd(NO_3)_2$ AND 0.10 *M* KNO_3

−log [Py]	Slope log $[(i_d/i) - 1]$ vs. $E_{1/2}$	$-E_{1/2}$ vs. s.c.e.	log K_{st}
1.226	0.034	0.580	1.52
1.100	.032	.582	1.49
1.002	.031	.585	1.49
0.874	.033	.589	1.48
.701	.033	.594	2.23
.588	.031	.600	2.19
.524	.031	.603	2.17
.302	.032	.615	2.14
.156	.033	.624	2.37
− .008	.032	.638	2.32
− .155	.032	.648	2.32
− .300	.033	.661	2.26

TABLE II
THERMODYNAMIC RESULTS FOR CADMIUM(II)–PYRAZOLE COMPLEXES

Reaction	Temp., °C.	*p*	log K_{st}	$-\Delta G°$, kcal./mole	$-\Delta H°$, kcal./mole
$Cd^{++} + Py = CdPy^{++}$	0	1.1	1.76	2.20	
	25	0.94	1.50	2.04	3.94
	45	0.96	1.28	1.86	
$Cd^{++} + 2Py = CdPy_2^{++}$	0	2.0	2.73	3.41	
	25	1.8	2.18	2.97	8.10
	45	1.8	1.80	2.62	
$Cd^{++} + 3Py = CdPy_3^{++}$	0	3.1	3.21	4.01	
	25	2.8	2.32	3.17	12.14
	45	2.9	1.83	2.66	
$Cd^{++} + 4Py = CdPy_4^{++}$		No formation observed			

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[5] D. Ilkovic, *Coll. Czech. Chem. Commun.*, **6**, 498 (1934).

[6] B. E. Douglas, H. A. Laitinen, and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **72**, 2484 (1950).

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Some Mono-*n*-alkylamino Derivatives of Hexachlorotriphosphonitrile

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The synthesis of monosubstituted pentachlorotriphosphonitriles has been of interest since de Fiquelmont[1] obtained the monoamido derivative by heating tetrachlorodiamidotriphosphonitrile with hydrogen chlo-

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[1] A. M. de Fiquelmont, *Ann. Chim.*, **12**, 169 (1939).