270 *Inorg. Chem.* **1987**, *26*, 270–272

The appreciable interaction between the phthalocyanine rings also results in significant (ca. 0.4 V) spacings between the successive oxidation waves; for negligible interactions, this spacing would be only about 36 mV.[20] The shift of the first reduction wave with increasing *n* is much less pronounced than that for the first oxidation wave, and the first two reduction waves of the trimer and tetramer are more closely spaced than the first two oxidation waves. These results provide a basis for further calculations of orbital energies in oligomers of this type.[18] The delocalization of charge in these cofacial phthalocyanine systems that is indicated by these results is consistent with the high conductivities observed with partially oxidized cofacial phthalocyanine polymers.[7,17]

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Oxidation of Hydrazine and Methyl-Substituted Hydrazines by the Cyano Complexes of Iron(III), Molybdenum(V), and Tungsten(V). A Kinetic Study

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Electron-transfer between the hydrazines and the cyano complexes of Fe(III), Mo(V), and W(V) in aqueous solution proceeds via an outer-sphere mechanism, and the rate data are consistent with the Marcus theory. The reactions are pH-dependent with a rate law $R = (k/(1 + [H^+]/K_a))[M(CN)_n{}^{3-}][\text{hydrazine}]$. From the kinetic data were obtained acid dissociation constants for the different hydrazines. Estimates of an upper limit of the $E°$ values for the different hydrazine couples, as well as a one-electron-self-exchange rate constant for the hydrazines, were obtained by application of the Marcus theory.

Introduction

The oxidation of hydrazine by several oxidizing agents has been the subject of a considerable amount of studies.[1] It was shown[2,3] that $N_2H_5^+$ is the reactive species in acidic media. The oxidation of hydrazine by $Mo(CN)_8{}^{3-}$, $W(CN)_8{}^{3-}$, and $Fe(CN)_6{}^{3-4}$ suggested that N_2H_4 is the reactive species in alkaline medium and that these rates of electron transfer are consistent with the Marcus theory.[5] The oxidation of hydrazine by the hexachloroiridate(IV) ion[6] was studied over a wide pH range (pH 1–10). The reaction rate was found to be pH-dependent and consistent with the rate law

$$R = \frac{k[IrCl_6{}^{2-}][N_2H_4]_T}{1 + [H^+]/K_a} \tag{1}$$

The hydrazinium radical, $N_2H_4^+$,[7] as well as N_2,[8,9] as reaction product has been identified, and the reaction mechanism, eq 2–4,

$$N_2H_5^+ \overset{K_a}{\rightleftharpoons} N_2H_4 + H^+ \tag{2}$$

$$IrCl_6{}^{2-} + N_2H_4 \xrightarrow{k} N_2H_4^+ + IrCl_6{}^{3-} \tag{3}$$

$$3IrCl^{2-} + N_2H_4^+ \xrightarrow[\text{fast}]{} N_2 + \text{products} \tag{4}$$

was proposed. An upper limit for the reduction potential of the $N_2H_4^+/N_2H_4$ couple has also been estimated as $E°(N_2H_4^+/N_2H_4) \leq 0.73$ V (vs. NHE) by considering electron transfer between $Fe(CN)_6{}^{3-}$ and N_2H_4. A self-exchange rate constant for the $N_2H_4^+/N_2H_4$ couple was calculated to be $\leq 3 \times 10^{-1}$ M^{-1} s^{-1}.

The previous study[4] and our present data yielded rate laws similar to that of the above-mentioned reaction. Since electron transfers in these reported studies are in support of an outer-sphere reaction pathway, the oxidations of the methyl-substituted hydrazines were studied for comparison with the hydrazine studies.

Experimental Section

$Cs_3Mo(CN)_8 \cdot 2H_2O$ and $Cs_3W(CN)_8 \cdot 2H_2O$ were prepared as described by Leipoldt et al.[10,11] and were used as primary standards[12] after recrystallization. All other reagents were of Merck "pro analisi" standard and were used as received. Hydrazinium sulfate, methylhydrazine, and 1,2-dimethylhydrazinium dichloride were used as sources of the hydrazinium species. Redistilled water was used throughout.

Table I. Kinetic, Structural, and Electrochemical Data for Reactants

couple	self-exchange rate const, M^{-1} s^{-1}	$E°$, V	r, Å	ref
$Mo(CN)_8{}^{3-}/Mo(CN)_8{}^{4-}$	3×10^4	0.76	4.8	27, 28, 24
$W(CN)_8{}^{3-}/W(CN)_8{}^{4-}$	7×10^4	0.54	4.8	27, 24
$Fe(CN)_6{}^{3-}/Fe(CN)_6{}^{4-}$	7×10^3	0.36	4.5	29, 27, 24
$IrCl_6{}^{2-}/IrCl_6{}^{3-}$	2×10^5	0.89	3.4	30
$N_2H_4^+/N_2H_4$	≤1.0	≤0.73	1.1	6, this work
$(CH_3)N_2H_3^+/(CH_3)N_2H_3$	≤1.0	≤0.62	1.5	this work
$(CH_3)HN_2H(CH_3)^+/$ $(CH_3)HN_2H(CH_3)$	≤1.0	≤0.56	1.8	this work

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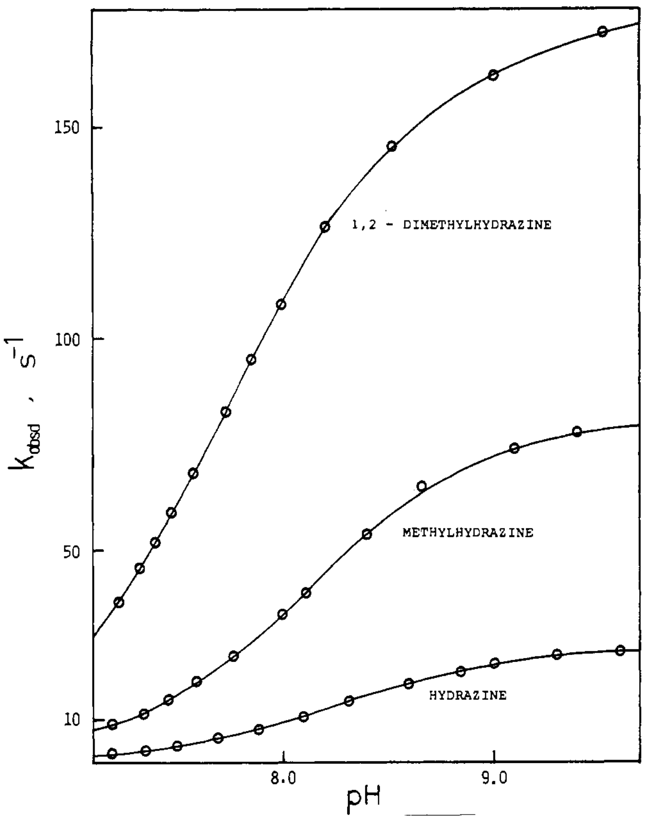

Figure 1. pH dependence for the oxidation of hydrazine, methylhydrazine, and 1,2-dimethylhydrazine by $Mo(CN)_8^{3-}$. $[Mo(CN)_8^{3-}] = 5 \times 10^{-4}$ M; $[N_2H_4] = 5 \times 10^{-3}$ M; $[(CH_3)N_2H_3] = [(CH_3)HN_2H(CH_3)] = 1.25 \times 10^{-3}$ M. $\mu = 0.1$ M (NaCl); $T = 15$ °C (solid lines by French curve).

The desired buffer solutions for varying the pH of the reaction medium were prepared by mixing suitable volumes of 0.2 M KH_2PO_4 or H_3BO_3 and 0.2 M KOH. The pH was measured with an Orion Research Model 701 pH meter.

Kinetic data were obtained by monitoring the decrease in the concentration of $Fe(CN)_6^{3-}$, $Mo(CN)_8^{3-}$, and $W(CN)_8^{3-}$ at 420, 390, and 357 nm, respectively, with a Durrum D-110 stopped-flow spectrophotometer. The concentration of the hydrazine species was stoichiometrically in excess by at least a factor of 10. Excellent pseudo-first-order plots were obtained. Experimental work was carried out in a darkened laboratory because solutions of $Mo(CN)_8^{3-}$ and $W(CN)_8^{3-}$ are sensitive to light.

Due to limitations of our equipment, the kinetic data for the reactions with the octacyanomolybdate(V) ion were collected at 15 °C and corrected to 25 °C by using eq 5. The activation energies, E_a, were obtained

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right) \tag{5}$$

from the Arrhenius equation, $\log k = -E_a/2.303RT$. From the observed data for variation of the temperature of reaction mixtures between 15 and 19 °C it was found that $E_a(Mo(CN)_8^{3-}/\text{hydrazine}) = 5.52$ kcal mol^{-1}, $E_a(Mo(CN)_8^{3-}/\text{methylhydrazine}) = 3.75$ kcal mol^{-1}, and $E_a(Mo(CN)_8^{3-}/\text{1,2-dimethylhydrazine}) = 3.90$ kcal mol^{-1}.

Results and Discussion

Kinetic measurements over a wide pH range for the reaction of $Mo(CN)_8^{3-}$ with the different hydrazine species (Figure 1) show the pH dependence of these reactions. Since the pK_{a3} values of the cyano complexes are below 3,[13,14] the main cyano species under the experimental conditions were the $M(CN)_n^{3-}$ ions. The observed pH dependence could thus only be attributed to equilibria of the type

$$R'HNNH_2R^+ \rightleftharpoons R'HNNHR + H^+ \tag{6}$$

Table II. Calculated[a] Work Terms and Observed Rate Constants[b] for the Oxidation of Hydrazines by the Cyano Complexes of Mo(V), W(V), and Fe(III)

no.	reaction	W_{11}, kcal	W_{21}, kcal	k_{obsd}, M^{-1} s^{-1}
1	$Fe(CN)_6^{3-} + N_2H_4$	2.92	−1.91	2.32 ± 0.02
2	$W(CN)_8^{3-} + N_2H_4$	2.65	−1.78	$(1.65 \pm 0.04) \times 10^2$
3	$Mo(CN)_8^{3-} + N_2H_4$	2.65	−1.78	$(1.1 \pm 0.2) \times 10^4$
4	$Fe(CN)_6^{3-} + (CH_3)N_2H_3$	2.92	−1.74	$(3.20 \pm 0.02) \times 10$
5	$W(CN)_8^{3-} + (CH_3)N_2H_3$	2.65	−1.62	$(1.78 \pm 0.04) \times 10^3$
6	$Mo(CN)_8^{3-} + (CH_3)N_2H_3$	2.65	−1.62	$(8.9 \pm 0.3) \times 10^4$
7	$Fe(CN)_6^{3-} + (CH_3)HN_2H(CH_3)$	2.92	−1.62	$(1.50 \pm 0.04) \times 10^2$
8	$W(CN)_8^{3-} + (CH_3)HN_2H(CH_3)$	2.65	−1.52	$(2.74 \pm 0.07) \times 10^3$
9	$Mo(CN)_8^{3-} + (CH_3)HN_2H(CH_3)$	2.65	−1.52	$(2.1 \pm 0.2) \times 10^5$
10	$IrCl_6^{2-} + N_2H_4$	2.19	−1.92	$(2.01 \pm 0.03) \times 10^4$[c]

[a] Parameters used are in Table I. $W_{22} = W_{12} = 0$. [b] Temperature = 25 °C; $[OH^-] = 0.05$ M. [c] From ref 6.

The pH dependence (Figure 1) and kinetic data obtained by the variation of the concentration of the different hydrazines in reaction mixtures are consistent with the rate law

$$\frac{-d[M(CN)_n^{3-}]}{dt} = \frac{k[M(CN)_n^{3-}][\text{hydrazine}]_T}{1 + [H^+]/K_a} \tag{7}$$

This suggests that the mechanism for these reactions is similar to eq 2–4. A nonlinear least-squares fit of the data to rate law 7 yielded $K_a(\text{hydrazine}) = 5.5 \times 10^{-9}$ M^{-1} ($pK_a = 8.3$), $K_a(\text{methylhydrazine}) = 7.5 \times 10^{-9}$ M^{-1} ($pK_a = 8.1$), and $K_a(\text{1,2-dimethylhydrazine}) = 1.8 \times 10^{-8}$ M^{-1} ($pK_a = 7.7$) under the approximation that $[H^+] = 10^{-pH}$ at 15 °C. The K_a values for hydrazine and methylhydrazine are in very good agreement with literature values[15-17] and also with the value obtained by Stanbury.[6] A comparative value for 1,2-dimethylhydrazine could not be found in the literature. The values for the cross-reaction rate constant, k_{12}, at high pH (0.05 M OH^-) where $[H^+] << K_a$ are given in Table II.

The kinetic results for the oxidation of hydrazine by $IrCl_6^{2-}$ [6] and the cyano complexes of Fe(III), W(V), and Mo(V)[4] were strongly in support of an outer-sphere reaction mechanism concerning a rate-determining one-electron-transfer (eq 3). A similar reaction pathway could be expected for the oxidation of the methyl-substituted hydrazines. This conclusion is supported by the fact that the data for the methyl-substituted hydrazines are also consistent with the Marcus theory as shown below.

In its simplest form, the Marcus relation (eq 8 and 9) predicts a linear relationship between the cross-reaction rate constant and the driving force of the reaction. Plots of $\log k_{obsd}$ for hydrazine,

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \tag{8}$$

$$\log f = (\log K_{12})^2/[4 \log (k_{11}k_{22}/Z^2)] \tag{9}$$

methylhydrazine, and 1,2-dimethylhydrazine vs. the respective $E°$ values for the cyano complexes were linear with slopes of 9.7, 8.6, and 8.0 V^{-1}, respectively. These agree very well with the expected slope of 8.46 V^{-1}, which shows that the results are consistent with the Marcus theory.

Margerum and co-workers have reported the self-exchange rates of a large number of copper[18] and nickel[19] peptide complexes to be similar. The different peptide complexes are α-carbon-substituted derivatives, and although the examples are for transition-metal complexes, it is reasonable to expect that the self-ex-

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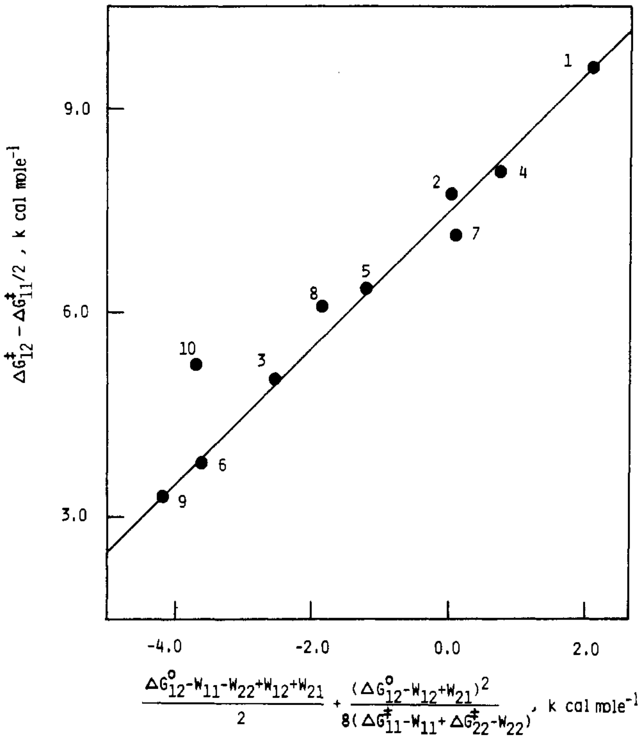

Figure 2. Marcus relation: Free energies of activation as a function of the driving force corrected for electrostatic work terms. μ = 0.1 M (NaCl); T = 25 °C (numbering as in Table II).

change rate constants for hydrazine and its methyl-substituted derivatives could also be similar. However, the large geometry changes that accompany the oxidation of hydrazine to its radical cation[20] implicate that nuclear tunneling should be a significant factor for N_2H_4 and $CH_3N_2H_3$ but not so much for $(CH_3)H\text{-}N_2H(CH_3)$ and that the electron-self-exchange rates for hydrazine and its methyl-substituted derivatives should thus not be equal.

Considering the unusual slow self-exchange rate for hydrazine,[21] it is, however, reasonable to assume that the nuclear tunneling effect can be neglected and that the self-exchange rates for hydrazine and its methyl-substituted derivatives would be fairly similar. This assumption and the fact that the kinetic data are consistent with the Marcus theory and also the availability of Stanbury's results make it possible to estimate upper limits for the $E°$ values of the methylhydrazine and 1,2-dimethylhydrazine couples. To accomplish this, a slope of 0.5 was forced through a plot of log k_{obsd} vs. log k_{12} for the oxidation of N_2H_4 by the cyano complexes of Fe(III), W(V), and Mo(V). From k_{obsd} for the reaction with the methyl-substituted hydrazines by interpolation and eq 10, upper limits for the reduction potentials (vs. NHE)

$$\log K = \frac{E°_{\text{oxidant}} - E°_{\text{reductant}}}{0.0591} \qquad (10)$$

of the redox couples $(CH_3)N_2H_3^+/(CH_3)N_2H_3$ and $(CH_3)HN_2H(CH_3)^+/(CH_3)HN_2H(CH_3)$ (an average from three reactions) were determined as $\leq$0.62 and $\leq$0.56 V, respectively, compared to $\leq$0.73 V for the $N_2H_4/N_2H_4^+$ couple.[6] This trend in the $E°$ values with increased methyl substitution on the N_2H_4 is in agreement with the better electron-donating ability of a methyl group relative to that of hydrogen.[22]

The Marcus theory (eq 8 and 9) assumes that the work terms required to bring the reactants together and separate the products are very similar or negligible for the self-exchange and cross-exchange processes and they cancel out in treatment. This assumption is not valid for reactions of the cyano complexes of Fe, W, and Mo. The large negative charges of these ions give rise to large electrostatic work terms that cannot be neglected.

The work terms have been calculated by the Debye–Hückel expression[23] (eq 11), where D is the absolute solvent dielectric,

$$W = Z_1Z_2e^2/Da(1 + \kappa a) \qquad (11)$$

κ is the reciprocal ionic layer thickness, and a is the distance of closest approach (sum of reactant radii). The reactant radii[21] for the cyano complexes are available in the literature and the radii for the hydrazine's were determined from eq 12,[23] where d_x, d_y,

$$r = \tfrac{1}{3}(d_xd_yd_z)^{1/3} \qquad (12)$$

and d_z are the molecular diameters along the three axes. The diameters of the hydrazines were estimated from stick and ball models, built from crystal structure data.[25,26]

The Marcus equation in terms of free energies of activation

$$\Delta G_{12}^* - W_{12} = \frac{(\Delta G_{11}^*-W_{11})+(\Delta G_{22}^*-W_{22})+(\Delta G_{12}°-W_{12}+W_{21})(1+\alpha)}{2} \qquad (13)$$

$$\alpha = \frac{\Delta G_{12}° - W_{12} + W_{21}}{4[(\Delta G_{11}^* - W_{11}) + (\Delta G_{22}^* - W_{22})]} \qquad (14)$$

predicts a linear relationship between

$$\Delta G_{12}^* - \Delta G_{11}^*/2$$

and

$$\frac{\Delta G_{12}° - W_{11} - W_{22} + W_{12} + W_{21}}{2} + \frac{(\Delta G_{12}° - W_{12} + W_{21})^2}{8(\Delta G_{11}^* - W_{11} + \Delta G_{22}^* - W_{22})}$$

with a slope of unity and intercept $\Delta G_{22}^*/2$ from which the self-exchange rate constant, k_{22}, can be obtained. A plot of this type for the oxidation of the hydrazines by the cyano complexes of Fe(III), W(V), and Mo(V) (Figure 2) is linear, and a forced slope of unity (after three iterations) yields the value $\Delta G_{22}^* \geq$ 15 kcal; therefore $k_{22} \leq$ 1.0 M^{-1} s^{-1}. This value is in good agreement with the value estimated by Stanbury.

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Registry No. $Fe(CN)_6^{3-}$, 13408-62-3; $W(CN)_8^{3-}$, 17568-76-2; $Mo(CN)_8^{3-}$, 17845-99-7; N_2H_4, 302-01-2; $(CH_3)N_2H_3$, 60-34-4; $(CH_3)HN_2H(CH_3)$, 540-73-8.

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