

The first reaction step is the penetration of the carboxylic group (in agreement with the much higher affinity of Fe(III) for carboxylic than for alcoholic groups) and then the chelation step occurs: the alcoholic oxygen coordinates the metal center and this link labilizes the alcoholic proton which is subsequently released. The chelation ring closure must be fast and not rate limiting as can be concluded by comparing the present results with those for monodentate carboxylic ligands (see for example the data for FeOH^{2+} -acetic acids reactions in Table IV).

Registry No. Glycolic acid, 79-14-1; DL-lactic acid, 598-82-3; DL-malic acid, 617-48-1; benzoic acid, 76-93-7; Fe(III), 20074-52-6.

References and Notes

- (1) R. G. Wilkins, "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes", Allyn and Bacon, Boston, 1974; D. Benson in "Comprehensive Chemical Kinetics", Vol. 16, C. H. Bamford and C. F. H. Tipper Eds., Elsevier, Amsterdam, 1975, Chapter 5.
- (2) E. Mentasti, E. Pelizzetti, and G. Saini, *J. Chem. Soc., Dalton Trans.*, 1944 (1974).
- (3) E. Mentasti, E. Pelizzetti, and G. Saini, *Gazz. Chim. Ital.*, **104**, 201 (1974).
- (4) E. Mentasti and E. Pelizzetti, *J. Chem. Soc., Dalton Trans.*, 2605 (1973).
- (5) E. Mentasti and E. Pelizzetti, *J. Inorg. Nucl. Chem.*, **38**, 785 (1976).
- (6) E. Mentasti, E. Pelizzetti, and C. Baiocchi, *Ann. Chim. (Rome)*, **66**, 407 (1976).
- (7) G. Wada and Y. Kobayashi, *Bull. Chem. Soc. Jpn.*, **48**, 2451 (1975).
- (8) R. M. Milburn, *J. Am. Chem. Soc.*, **79**, 537 (1957).
- (9) C. Bertin Batsch, *Ann. Chim. (Paris)*, **7**, 481 (1952).
- (10) A. D. Gilmour and A. McAuley, *J. Chem. Soc. A*, 2345 (1969).
- (11) A. Miftahova, L. Dozsa, and M. T. Beck, *Acta Chim. Acad. Sci. Hung.*, **92**, 379 (1977).
- (12) (a) H. Bobtelsky and J. Jordan, *J. Am. Chem. Soc.*, **67**, 1824 (1945); (b) R. C. Warner and J. Weber, *ibid.*, **75**, 5086 (1953); (c) K. S. Rajan and A. E. Martell, *J. Inorg. Nucl. Chem.*, **26**, 1927 (1964); (d) S. B. Hanna and S. A. Sarac, *J. Org. Chem.*, **42**, 2069 (1977).
- (13) A. E. Martell and L. G. Sillën, *Chem. Soc., Spec. Publ.*, No. **17** (1964); No. **25** (1971).
- (14) S. Gouger and J. Stuehr, *Inorg. Chem.*, **13**, 379 (1974).
- (15) (a) B. Permuter-Hayman and E. Tapuhi, *J. Coord. Chem.*, **6**, 31 (1976); (b) *ibid.*, **8**, 75 (1978).
- (16) D. Pouli and W. M. Smith, *Can. J. Chem.*, **40**, 1836 (1962).
- (17) D. W. Carlyle and J. H. Espenson, *Inorg. Chem.*, **6**, 1370 (1967).
- (18) F. P. Cavasino, *J. Phys. Chem.*, **72**, 1378 (1968).
- (19) F. Accascina, F. P. Cavasino, and E. Di Dio, *Trans. Faraday Soc.*, **65**, 489 (1969).
- (20) J. H. Espenson and D. F. Dustin, *Inorg. Chem.*, **8**, 1760 (1969).
- (21) F. P. Cavasino and E. Di Dio, *J. Chem. Soc. A*, 1151 (1970).
- (22) G. Saini and E. Mentasti, *Inorg. Chim. Acta*, **4**, 210 and 585 (1970).
- (23) U. D. Gomwalk, A. G. Lappin, J. P. McCann, and A. McAuley, *Inorg. Chim. Acta*, **24**, 39 (1977).
- (24) N. Kujundzic and M. Pribanic, *J. Inorg. Nucl. Chem.*, **40**, 729 (1978).
- (25) M. Eigen and R. G. Wilkins, *Adv. Chem. Ser.*, No. **49**, 55 (1965); see also M. Eigen, *Pure Appl. Chem.*, **6**, 97 (1963); **20**, 93 (1969); A. McAuley and J. Hill, *Q. Rev., Chem. Soc.*, **23**, 18 (1969).
- (26) J. E. Pure, *J. Chem. Soc.*, 7534 (1965).
- (27) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).
- (28) D. Seewald and N. Sutin, *Inorg. Chem.*, **2**, 643 (1963).

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Composition and Kinetics of the Complex Formed by the Interaction of Chromium(III) with *p*-Hydroxybenzoic Acid

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The composition of the complex formed by the interaction of solutions of chromium(III) and *p*-hydroxybenzoic acid was determined by using Job's method of continuous variations in aqueous ethanolic medium. The reaction was found to be slow, and the kinetic studies were carried out under varying conditions of temperature, hydrogen ion concentration, solvent composition, and ligand concentration. The pseudo-first-order rate constants (k_{obsd}) were found to follow the equation $k_{\text{obsd}} = k_{\text{an}}K_1K_a[\text{AH}]_{\text{T}}/([\text{H}^+] + K_a + K_1K_a[\text{AH}]_{\text{T}})$. A possible mechanism of the associative interchange (I_a) type was proposed. The activation parameters are $\Delta H_{\text{an}}^* = 105 \pm 1 \text{ kJ mol}^{-1}$ and $\Delta S_{\text{an}}^* = 25 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$ for anation and $\Delta H_{\text{IP}}^{\circ} = -52 \pm 8 \text{ kJ mol}^{-1}$ and $\Delta S_{\text{IP}}^{\circ} = -159 \pm 25 \text{ J K}^{-1} \text{ mol}^{-1}$ for ion pairing.

Swaddle and King^{1,2} have discussed the proton ambiguity involved in the substitution reactions of chromium(III) for the aquation of CrF^{2+} and CrN_3^{2+} complexes. Espenson³ has reported the same type of ambiguity for the anation reactions of hexaquo chromium(III) with various weak and strong acids and concluded that kinetic studies will not differentiate between the two pathways, since they correspond to transition states of the same composition. Later Thusius⁴ studied the rate of formation of monosubstituted chromium(III) complexes and supported the conclusion reached by Espenson³ on the basis of activation parameters and the ratios of the rate constants for the anation and the water-exchange reactions. Swaddle⁵ has reviewed many possibilities of proton participation in the substitution reactions of hexaquo chromium(III). In continuation of our studies on the anation reactions of chromium(III) with oxygen- and nitrogen-containing organic ligands, the work on the interaction of hexaquo chromium(III) with *p*-hydroxybenzoic acid in aqueous ethanolic medium is reported here.

Experimental Section

Stock solutions of chromium nitrate, sodium nitrate, sodium hydroxide, and nitric acid were prepared from AR grade reagents. *p*-Hydroxybenzoic acid (Riedel-De Haenag, Seelze-Hannover) was used as such. Absolute ethanol was prepared as described by Vogel.⁶

Chromium nitrate solution was standardized by the ion-exchange method.⁷ All the solutions were prepared in aqueous ethanol (mole fractions of ethanol = 0.09, 0.23, and 0.48).

The composition of the complex formed by the interaction of chromium(III) and *p*-hydroxybenzoic acid was determined by Job's method of continuous variations. The optical density measurements were made at 580 nm with a Bausch and Lomb Spectronic-20. The pH measurements were made with a Titrierautomat, Type AT-2, by a suitable correction for solvent composition.⁸

The kinetic measurements for the reaction of *p*-hydroxybenzoic acid with chromium(III) were carried out by mixing the solutions in a two-necked flask fitted with a double-walled condenser. The reaction flask was kept in a thermostat-controlled bath at the desired temperature within ± 0.1 °C. The final concentration of chromium nitrate in the reaction vessel was $4.0 \times 10^{-3} \text{ M}$ and that of *p*-hydroxybenzoic acid was varied from 0.04 to 0.16 M. Nitrogen gas was bubbled through the reaction mixture for stirring and in order to maintain an inert atmosphere. The ionic strength of the reaction mixture was adjusted with sodium nitrate solution. The progress of reaction was followed spectrophotometrically at 580 nm. The pseudo-first-order rate constants (k_{obsd}) and other parameters were calculated by using an IBM 1130 computer.

Results and Discussion

It was found by Job's method of continuous variations that 1 mol of *p*-hydroxybenzoic acid reacts with 1 mol of chromium(III). The composition of the complex was not affected

Table I. Values of Rate Parameters Based on Eq 5 at Different Temperatures^a

temp, °C	$10^4 k_{an}, s^{-1}$	K_I, M^{-1}	$10^3 K_a, M$	$10^5 rms^b$	$10^5 k_{H_2O},^c s^{-1}$	$10^5 k_{EtOH},^d s^{-1}$
25	1.1 (± 0.0)	7.4 (± 0.4)	0.76 (± 0.04)	0.49		
30	2.1 (± 0.1)	5.6 (± 0.3)	0.99 (± 0.05)	0.94		
35	4.9 (± 0.2)	4.4 (± 0.2)	1.2 (± 0.1)	2.5	0.42	
39.6						2.2
40	8.5 (± 2.6)	2.6 (± 0.3)	1.3 (± 0.2)	7.8		

^a $[H^+] = 0.19 \times 10^{-2} M$, $\mu = 1.0$, and the mole fraction of ethanol = 0.23. Error limits are standard deviations. ^b Root-mean-square deviations between observed and calculated values of pseudo-first-order rate constants. ^c From ref 9. ^d From ref 10.

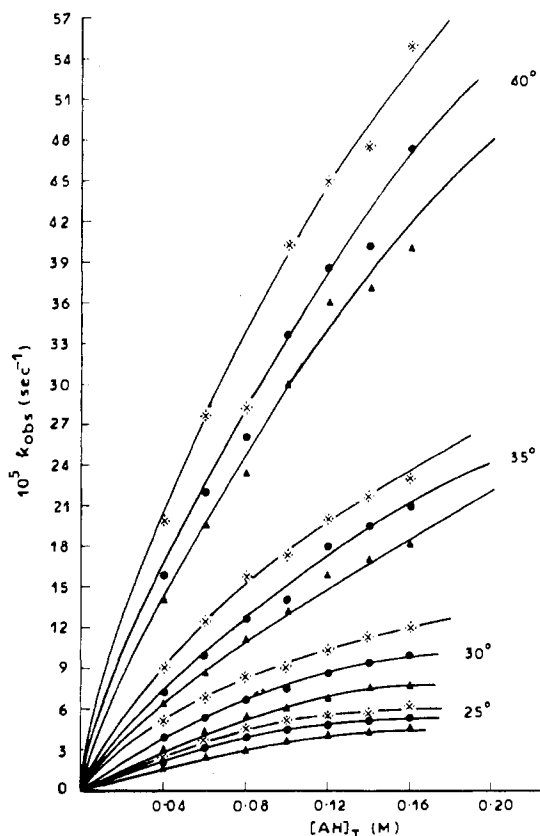
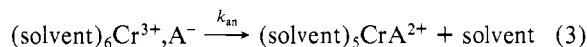
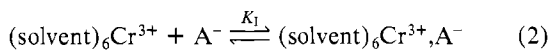
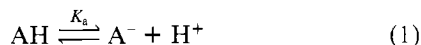


Figure 1. Dependence of k_{obsd} on $[AH]_T$ at the indicated temperatures with $\mu = 1.0$, mole fraction of ethanol = 0.23, and $[H^+] = 0.03 \times 10^{-2} M$ (*), $0.19 \times 10^{-2} M$ (●), and $0.38 \times 10^{-2} M$ (▲).

by the composition of the aqueous ethanolic medium.

The pseudo-first-order rate constants (k_{obsd}) were determined at different hydrogen ion and ligand concentrations at 25, 30, 35, and 40 °C. The results are given in Figure 1. The dependence of k_{obsd} on ligand and hydrogen ion concentrations is consistent with an ion-pair mechanism which may be represented by eq 1-3, and the rate equation derived on the



basis of the above mechanism is given by eq 4, where $[AH]_T$

$$\frac{d \ln [\text{complex}]}{dt} = k_{obsd} = \frac{k_{an} K_I K_a [AH]_T}{[H^+] + K_a + K_I K_a [AH]_T} \quad (4)$$

is the total concentration of *p*-hydroxybenzoic acid added. On rearrangement eq 4 gives eq 5, which satisfies the observed results (Figure 2).

$$\frac{1}{k_{obsd}} = \frac{1}{k_{an}} + \frac{K_a + [H^+]}{k_{an} K_I K_a} \frac{1}{[AH]_T} \quad (5)$$

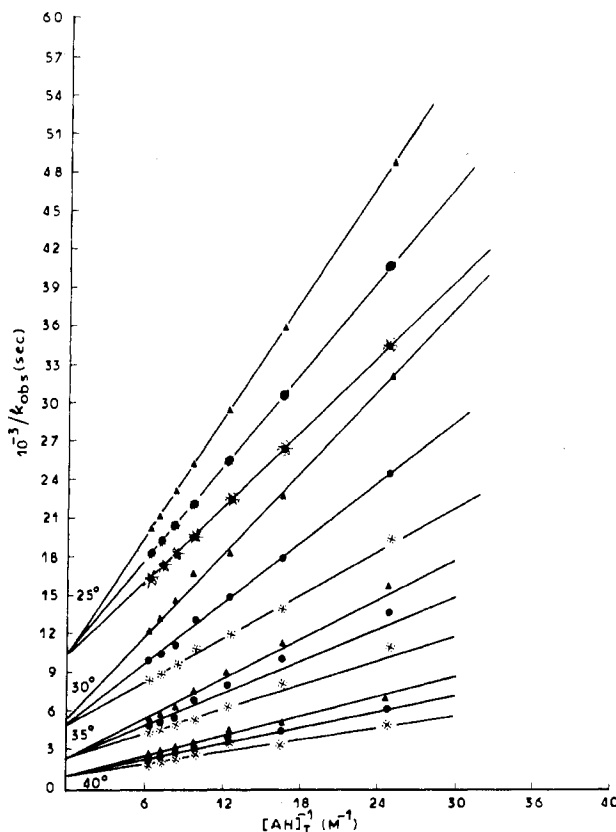


Figure 2. Linear dependence of k_{obsd}^{-1} on $[AH]_T^{-1}$ at the indicated temperatures with $\mu = 1.0$, mole fraction of ethanol = 0.23, and $[H^+] = 0.03 \times 10^{-2} M$ (*), $0.19 \times 10^{-2} M$ (●), and $0.38 \times 10^{-2} M$ (▲). The lines show calculated values and the points are observed values.

The values of the rate parameters of eq 5 were calculated by linear least-squares regression analysis and are summarized in Table I. The values of k_{an} in aqueous ethanol (mole fractions of ethanol = 0.09, 0.23, and 0.48) at 35 °C with $\mu = 1.0$ and $[H^+] = 0.19 \times 10^{-2} M$ were calculated and found to be $5.7 (\pm 1.0) \times 10^{-4} s^{-1}$, $4.9 (\pm 0.2) \times 10^{-4} s^{-1}$, and $3.3 (\pm 0.4) \times 10^{-4} s^{-1}$, respectively. The values of the activation parameters as given by the Eyring equation under these conditions are $\Delta H_{an}^* = 105 \pm 1 kJ mol^{-1}$ and $\Delta S_{an}^* = 25 \pm 3 J K^{-1} mol^{-1}$ for anation and $\Delta H_{IP}^* = -52 \pm 8 kJ mol^{-1}$ and $\Delta S_{IP}^* = -159 \pm 25 J K^{-1} mol^{-1}$ for ion pairing. It is clear from Table I that the values of k_{an} are far greater than those of water or ethanol exchange and suggest ligand-assisted anation. The lower enthalpy of activation for anation ($\Delta H_{an}^* = 105 \pm 1 kJ mol^{-1}$) than for solvent exchange^{9,10} ($\Delta H_{H_2O}^* = 108 kJ mol^{-1}$ and $\Delta H_{EtOH}^* = 100-112 kJ mol^{-1}$) shows that the anation step depends upon the nature of the ligand and confirms the associative interchange (I_a) type mechanism.

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Registry No. *p*-Hydroxybenzoic acid, 99-96-7; Cr³⁺, 16065-83-1.

References and Notes

- (1) Swaddle, T. W.; King, E. L. *Inorg. Chem.* **1964**, *3*, 234.
- (2) Swaddle, T. W.; King, E. L. *Inorg. Chem.* **1965**, *4*, 532.
- (3) Espenson, J. H. *Inorg. Chem.* **1969**, *8*, 1554.
- (4) Thusius, D. *Inorg. Chem.* **1971**, *10*, 1106.
- (5) Swaddle, T. W. *Coord. Chem. Rev.* **1974**, *14*, 217.
- (6) Vogel, A. I. "A Text Book of Practical Organic Chemistry"; Longmans, Green and Co.: London, 1956; p 166.
- (7) Benerjea, D.; Chaudhuri, S. D. *J. Inorg. Nucl. Chem.* **1968**, *30*, 871.
- (8) Bates, R. G. "The Determination of pH"; Wiley: New York, 1954; p 150.
- (9) Plane, R. A.; Taube, H. *J. Phys. Chem.* **1952**, *56*, 33.
- (10) Kemp, D. W.; King, E. L. *J. Am. Chem. Soc.* **1967**, *89*, 3433.

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Synthesis and Kinetics of Formation and Aquation of cis-Bis(oxalato)bis(dimethylformamide)chromate(III)

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The isolation by ion-exchange chromatography of *cis*-Cr(C₂O₄)₂(HCON(CH₃)₂)₂⁻ has been effected. The complex has visible maxima at 418 and 565 nm with molar absorptivities of 87.5 and 96.5 M⁻¹ cm⁻¹, respectively. The aquation of this compound occurred in consecutive first-order reactions with the first step corresponding to the replacement of the first HCON(CH₃)₂ and the second step corresponding to the replacement of the second HCON(CH₃)₂. The intermediate was concluded to be *cis*-Cr(C₂O₄)₂(HCON(CH₃)₂)(OH₂)⁻. The reactions are independent of pH between pH 1 and 5 with $k_1 = (6.95 \pm 0.28) \times 10^{-4} \text{ s}^{-1}$ and $k_2 = (3.27 \pm 0.18) \times 10^{-4} \text{ s}^{-1}$ at 25 °C and $\mu = 1.00 \text{ M}$ (NaNO₃). The activation parameters are $\Delta H^\ddagger = 14.3 \pm 0.4$ and 14.2 ± 0.9 kcal/mol and $\Delta S^\ddagger = -24.9 \pm 1.3$ and -26.9 ± 3.0 cal/(deg mol) for the first and second steps, respectively. An I_a mechanism was assigned for both steps. The solvolysis reaction of *cis*-Cr(C₂O₄)₂(OH₂)₂⁻ in HCON(CH₃)₂ is very similar to the aquation reaction. The value of k_{-2} (first step) is $(1.75 \pm 0.04) \times 10^{-3} \text{ s}^{-1}$ and k_{-1} (second step) is $(1.87 \pm 0.05) \times 10^{-4} \text{ s}^{-1}$ at 25 °C. The values of the activation parameters are $\Delta H^\ddagger = 14.4 \pm 0.2$ and 14.7 ± 0.3 kcal/mol and $\Delta S^\ddagger = -22.8 \pm 0.7$ and -26.1 ± 0.9 cal/(deg mol) for the first and second steps, respectively. The equilibrium behavior was studied at 25 °C, [H⁺] = 10⁻³ M, and $\chi_{\text{DMF}} = 0.028\text{--}0.90$ in aqueous dimethylformamide solutions. The equilibrium quotients are $Q_1 = 5.55 \pm 0.27$ and $Q_2 = 0.437 \pm 0.069$.

Introduction

The mechanism of the reactions of the *cis*-Cr(C₂O₄)₂ moiety have been of continuing interest. The complexes involving the monodentate ligands (CH₃)₂SO,¹ CH₃COO⁻,² NCS⁻,³ N₃⁻,⁴ C₅H₅N,^{2,5} and CN⁻^{6,7} have been studied. With the exception of (CH₃)₂SO, all of the complexes were in aqueous solutions, and the aquation reactions only were studied. With (CH₃)₂SO, both H₂O and (CH₃)₂SO were used as solvents, and both the aquation and solvolysis reactions were studied. The results implied that the reactions of *cis*-Cr(C₂O₄)₂(OH₂)Lⁿ⁻, where L is (CH₃)₂SO, CH₃COO⁻, NCS⁻, and N₃⁻, occurred by an I_a mechanism.⁴ That is, the rate constants and activation parameters for aquation are relatively insensitive to the nature of the leaving group. However, only the equilibrium constant with NCS⁻ has been determined.

In the effort to better understand this system, the present investigation was undertaken. The reactions of the *cis*-Cr(C₂O₄)₂ moiety with HCON(CH₃)₂(DMF) were studied. Both aquation and solvolysis reactions were investigated. This paper presents the results.

Experimental Section

Chemicals and Instruments. All chemicals used were reagent, analytical, or primary-standard grade, depending upon the need. Mallinckrodt AR grade dimethylformamide was used. Before being used, it was vacuum distilled from anhydrous barium oxide or Davison 4A molecular sieves. The ion-exchange resin was 200–400 mesh Bio-Rad Ag 1-X8 anion-exchange resin in the nitrate form. The instrumentation has been described before.⁴

Analytical Methods. The analyses for chromium were performed as previously described.⁸ For the analyses of DMF, a solution containing about 0.50 mmol of DMF was hydrolyzed to dimethylamine with 5 mL of 1.0 M H₂SO₄ at 60 °C for 1 h. The solution was cooled and made basic with 10 mL of 3.6 M KOH. The dimethylamine was distilled from the basic solution into 2 mL of 0.48 M HCl. The resulting dimethylamine solution was analyzed spectrophotometrically by a method described by Cullis and Waddington.⁹ The ion-exchange

techniques have been described.¹⁰

Preparation of Compounds. The sodium *trans*-bis(oxalato)diaquochromate(III) was prepared by the method described by Werner.¹¹ Sodium *cis*-bis(oxalato)bis(dimethylformamide)chromate(III) was prepared by adding 10 g of sodium *trans*-bis(oxalato)diaquochromate(III) to 70 mL of DMF. The temperature was raised to 90 °C and maintained for 4 h. The solution was cooled to room temperature and kept in the refrigerator overnight. The crystals that formed were collected on a filter and washed with absolute ethanol and anhydrous diethyl ether. The product was recrystallized by dissolving 10 g of the product in 50 mL of DMF at 90 °C. The solution was cooled to room temperature and kept in the refrigerator overnight. The crystals that formed were collected and treated as before. The final product was dried for 6 h in a vacuum desiccator at 20 torr at room temperature. Attempts to isolate *cis*-Cr(C₂O₄)₂(HCON(CH₃)₂)(OH₂)⁻ by using ion-exchange chromatography at 1 °C were unsuccessful. The complexes aquated on the column too fast to be separated by this technique. Both very fast and very slow elution rates were used.

Equilibrium Measurements. The values of \bar{n} , the average number of DMF molecules bound to chromium, as a function of χ_{DMF} were determined in the following manner. A series of solutions of DMF and H₂O with χ_{DMF} from 0.028 to 0.90 containing about 0.01 M *cis*-Cr(C₂O₄)₂(HCON(CH₃)₂)₂⁻ were equilibrated for 24 h at 25 °C. Then, 5 mL of each solution was added to an anion-exchange column. The column capacity was about 10 mequiv. The solution was run into the column, and 15 mL of ice-cold H₂O was passed through the column. Blank experiments established that this would remove all of the solvent DMF. The 1- complexes were eluted then with ice-cold 0.10 M NaNO₃. The complete time required for this separation was about 5 min. The eluted solutions were analyzed for chromium and DMF as described above.

Kinetic Measurements. The kinetic runs were made on a Cary 11 or 15 recording spectrophotometer. Both instruments were fitted with 10-cm constant-temperature cell blocks that maintained the temperature to within ± 0.1 °C of that desired. The change in absorbance was measured at 565 nm. The pH was adjusted with HNO₃ and $\mu = 1.00 \text{ M}$ (NaNO₃). The complex concentration was 0.50 mM. In the solvolysis reactions and in the reactions in DMF–H₂O solutions,