Table III. pH Effects on Quantum Yields

Solvent	ϕ_{NH_3}	ϕ_F	ϕ_{NH_3}/ϕ_F
0.10 M $HClO_4$	0.47	0.0044	107
0.010 M $HClO_4$	0.44	0.0042	105
H_2O	0.64	0.011	58

The pH effects are summarized in Table III. Changing the pH of the medium from 2 to 1 did not appear to effect the quantum yields significantly for either ammonia or fluoride loss, although the slight increase in ϕ_{NH_3} may be real. However, when photolyzed in neutral solution, a significant increase in both quantum yields was observed. The thermal aquation rate constant is independent of pH from 1 to 10.5.[8] A similar pH behavior was observed in the photochemistry of $Co(NH_3)_5F^{2+}$, although the effect was not as large.[18] The enhancement of quantum yields in neutral solution emphasizes the importance of treating the excited state as a separate chemical species capable of its own acid–base chemistry.

Registry No. $[Cr(NH_3)_5F](ClO_4)_2$, 22478-31-5.

References and Notes

(1) E. Zinato in "Concepts of Inorganic Photochemistry", A. W. Adamson and P. D. Fleischauer, Ed., Wiley, New York, N.Y., 1975.
(2) C. Kutal and A. W. Adamson, *J. Am. Chem. Soc.*, **93**, 5581 (1971).
(3) S. Pyke and R. G. Linck, *J. Am. Chem. Soc.*, **93**, 5281 (1971).
(4) A. D. Kirk, K. C. Moss, and J. G. Valentine, *Can. J. Chem.*, **48**, 1524 (1971).
(5) See D. A. Rowley, *Inorg. Chem.*, **10**, 397 (1971), and references therein.
(6) J. I. Zink, *J. Am. Chem. Soc.*, **94**, 8039 (1972).
(7) See also G. Wirth and R. G. Linck, *J. Am. Chem. Soc.*, **95**, 5913 (1973), on results for *trans*-$Cr(en)_2ClF^+$.
(8) T. P. Jones and J. K. Phillips, *J. Chem. Soc. A*, 674 (1968).
(9) M. Mori, *Inorg. Synth.*, **5**, 132 (1957).
(10) E. Zinato, R. Lindholm, and A. W. Adamson, *J. Inorg. Nucl. Chem.*, **31**, 449 (1969).
(11) W. T. Bolleter, C. J. Buchman, and P. W. Tidwell, *Anal. Chem.*, **33**, 592 (1961).
(12) S. Megregian in "Colorimetric Determination of Nonmetals", D. F. Boltz, Ed., Interscience, New York, N.Y., 1958.
(13) E. Wegner and A. W. Adamson, *J. Am. Chem. Soc.*, **88**, 394 (1966).
(14) See also T. L. Allen, *Anal. Chem.*, **30**, 447 (1958).
(15) The result for ϕ_{NH_3} is in agreement with independent work done by C. F. C. Wong and A. D. Kirk, where ϕ_{NH_3} was found to be 0.43; A. D. Kirk, private communication.
(16) E. Zinato, P. Riccieri, and A. W. Adamson, *J. Am. Chem. Soc.*, **96**, 375 (1974); see also C. F. C. Wong and A. D. Kirk, *Inorg. Chem.*, **15**, 1519 (1976).
(17) A. D. Kirk, private communication.
(18) R. A. Pribush, C. K. Poon, C. M. Bruce, and A. W. Adamson, *J. Am. Chem. Soc.*, **96**, 3027 (1974).

Contribution from the Department of Chemistry,
The Pennsylvania State University,
University Park, Pennsylvania 16802

Pyrolysis of Aminophosphazenes[1]

H. R. Allcock,* C. H. Kolich, and W. C. Kossa

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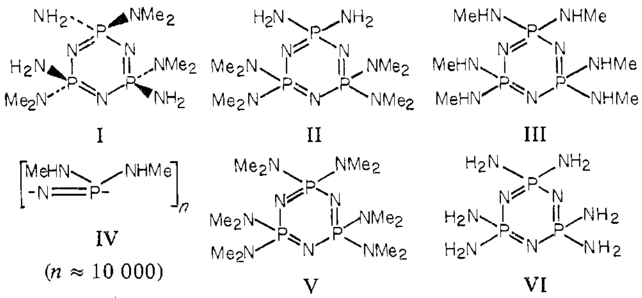
A large number of aminophosphazenes have been synthesized by the interaction of halocyclophosphazenes with primary or secondary amines.[2] The thermal behavior of this class of compounds is of some interest since specific aminocyclophosphazenes are useful as flame retardants and others have a biomedical significance.[3-5]

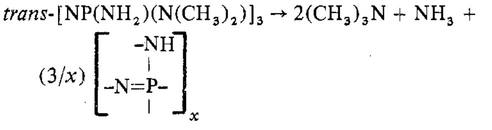
In this note we report the behavior of five specific aminophosphazenes (I–V) at elevated temperatures.



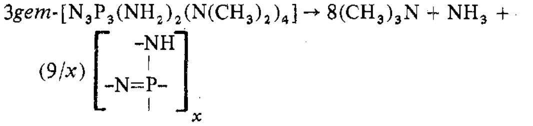
I II III IV ($n \approx$ 10 000) V VI

Those cyclo- or polyphosphazenes which contained both $-NH_2$ and $-NMe_2$ groups (I and II) or $-NHMe$ groups (III and IV) yielded trimethylamine and ammonia as volatile pyrolysis products. Compound V yielded only trimethylamine, and compound VI was reported to yield ammonia.[6] The residual products were phospham-type species in each case. Rapid thermal decomposition studies showed that those compounds which contained $-NMe_2$ groups initially evolved dimethylamine, while those which contained $-NHMe$ groups yielded monomethylamine. However, these products are thermodynamically unstable at 300 °C with respect to conversion to trimethylamine and ammonia.[7]

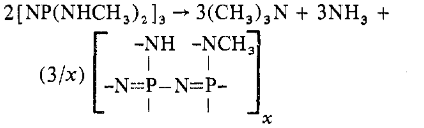
Table I lists the amounts of volatile pyrolysis products obtained at 310 °C from the aminophosphazenes studied, together with comparative published data for $[NP(NH_2)_2]_3$ (VI). These results are incorporated into eq 1–6.



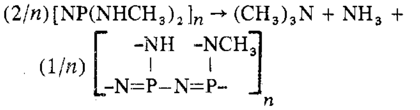
$$trans\text{-}[NP(NH_2)(N(CH_3)_2)]_3 \rightarrow 2(CH_3)_3N + NH_3 + (3/x)\left[\begin{array}{c} -NH \\ | \\ -N{=}P- \\ | \end{array}\right]_x \tag{1}$$



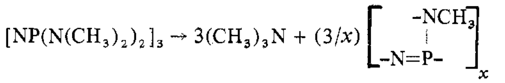
$$3gem\text{-}[N_3P_3(NH_2)_2(N(CH_3)_2)_4] \rightarrow 8(CH_3)_3N + NH_3 + (9/x)\left[\begin{array}{c} -NH \\ | \\ -N{=}P- \\ | \end{array}\right]_x \tag{2}$$



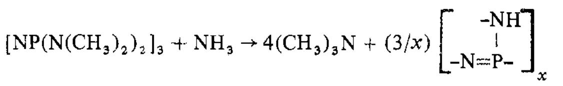
$$2[NP(NHCH_3)_2]_3 \rightarrow 3(CH_3)_3N + 3NH_3 + (3/x)\left[\begin{array}{cc} -NH & -NCH_3 \\ | & | \\ -N{=}P- & N{=}P- \\ | & | \end{array}\right]_x \tag{3}$$



$$(2/n)[NP(NHCH_3)_2]_n \rightarrow (CH_3)_3N + NH_3 + (1/n)\left[\begin{array}{cc} -NH & -NCH_3 \\ | & | \\ -N{=}P- & N{=}P- \end{array}\right]_n \tag{4}$$

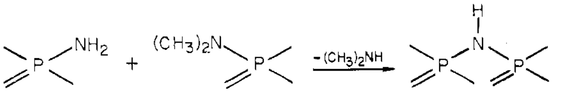


$$[NP(N(CH_3)_2)_2]_3 \rightarrow 3(CH_3)_3N + (3/x)\left[\begin{array}{c} -NCH_3 \\ | \\ -N{=}P- \end{array}\right]_x \tag{5}$$



$$[NP(N(CH_3)_2)_2]_3 + NH_3 \rightarrow 4(CH_3)_3N + (3/x)\left[\begin{array}{c} -NH \\ | \\ -N{=}P- \end{array}\right]_x \tag{6}$$

Those compounds that contained both $-NH_2$ and $-N(CH_3)_2$ substituent groups condensed to form a phospham-like product by the reaction shown in eq 7. On the other hand, the



$$>P-NH_2 + (CH_3)_2N-P< \xrightarrow{-(CH_3)_2NH} >P-\overset{H}{N}-P< \tag{7}$$

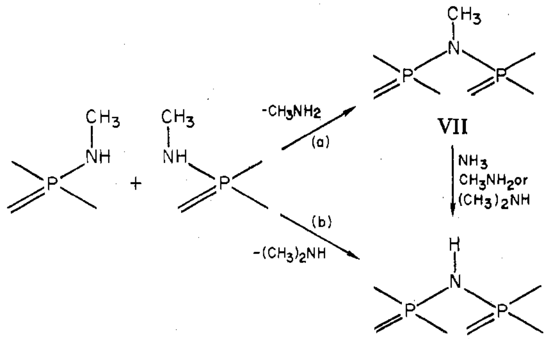
methylaminophosphazenes III and IV could undergo condensation–polymerization by two alternative pathways, as shown in (a) and (b) in Scheme I. Pathway (a) would appear to represent the actual reaction preference since monomethylamine was the only volatile product produced in the *initial* stages of the reaction. However, the actual conversion of an $-N(CH_3)-$ cross-link (VII) to an $-N(H)-$ linkage (VIII) could occur in the presence of ammonia, methylamine, or dimethylamine with the concurrent loss of methylamine, dimethylamine, or trimethylamine. At least two of the three

Table I. Thermal Decomposition Data for Aminophosphazenes at 310 °C after 89 h

	Amt, mmol					
Reactant	Phosphazene	$(CH_3)_3N$	NH_3	Total gaseous product	$(CH_3)_3N:NH_3$	% decompn[a]
I	0.916	1.69	0.73	2.42	2.3	88
II	1.162	3.11	0.30	3.41	10.5	98
III	0.939	1.41	1.16	2.57	1.2	91
IV[b]	3.34/n	1.58	1.64	3.22	0.96	96
V	0.840	0.062		0.062		2.5
V	0.675	0.39	1.15[c]	1.54		14
VI[d]	4.47		12.06	12.06		90

[a] Based on total amount of gaseous product. [b] The degree of polymerization, n, was estimated to be ~10 000–15 000. [c] Initially 1.94 mmol of ammonia was sealed in the vessel with the phosphazene. [d] Data from ref 8.

Scheme I



VIII

reactions, (a), (b), or (c), must be invoked to account for the observation that approximately equal numbers of $-N(CH_3)-$ and $-N(H)-$ cross-links were detected (by infrared and microanalytical analysis) in the decomposition residues from III and IV.

Compound V was surprisingly stable to thermal degradation at 310 °C.[9] However, the introduction of ammonia into the system accelerated the decomposition by a factor of more than 5. This was taken as evidence that ligand exchange of amino residues can occur at elevated temperatures, followed by pyrolytic condensation of the NH_2-group-containing products.

The insoluble, infusible residues from all the thermal decompositions gave nearly identical infrared spectra (see Experimental Section). These spectra were very similar to that reported for the phospham produced by the thermal degradation of VI.[6,8] The reactions reported here also show similarities to those described for the pyrolysis of anilinocyclophosphazenes.[10]

The experimental data suggest the following qualitative order of ligand thermal stability for phosphazenes that contain amino substituents: $-N(CH_3)_2 > -NHCH_3 > -NH_2$. It is important to note that the decomposition and cross-linking pathway reported here for $[NP(NHCH_3)_2]_n$ contrasts markedly with the cyclization–depolymerization pathways observed for fluoroalkoxy or aryloxyphosphazene high polymers, such as $[NP(OCH_2CF_3)_2]_n$ and $[NP(OC_6H_5)_2]_n$.[11,12] These species undergo only minimal side-group reactions at elevated temperatures,[13] and the thermolysis products are the analogous cyclic trimers and higher cyclic oligomers.

Experimental Section

Syntheses. The following aminophosphazenes were synthesized by procedures already reported in the literature: $[NP(NHCH_3)_2]_3$ (III), mp 257–259 °C;[14] $[NP(NHCH_3)_2]_n$ (IV);[4] $[NP(N(CH_3)_2)_2]_3$ (V), mp 103–105 °C.[14] *gem*-$N_3P_3(NH_2)_2[N(CH_3)_2]_4$ (II), mp 144–146 °C, was synthesized by dimethylaminolysis of *gem*-$N_3P_3(NH_2)_2Cl_4$, mp 161–164 °C,[15] in diethyl ether.

The hitherto unreported compound 1,*trans*-3,*trans*-5-triamino-1,3,5-tris(dimethylamino)cyclotriphosphazene (I) was synthesized by the following procedure. Liquid dimethylamine (406 g, 9.00 mol) was added during 1 h to a cooled, stirred solution of hexachlorocyclotriphosphazene (522 g, 1.50 mol) and diethyl ether (6000 mL) maintained at -78 °C. Stirring was continued for a further 6 h, after which time the reaction mixture was allowed to stand at 25 °C for 12 h. Precipitated dimethylammonium chloride was removed by filtration, and solvent was removed from the clear, colorless filtrate under reduced pressure to yield a white, solid residue. This was recrystallized from *n*-hexane to give 1,*trans*-3,*trans*-5-trichloro-1,3,5-tris(dimethylamino)cyclotriphosphazene (330 g, 58.8%), mp 101–104 °C (lit. mp 105 °C).[14]

This product (164 g, 0.438 mol) was dissolved in tetrahydrofuran (~300 mL) and the solution was placed in a stainless-steel autoclave. Liquid ammonia (~200 mL) was added carefully, the autoclave was sealed, and the mixture was stirred at 25 °C for 24 h. The contents of the autoclave were transferred to a vacuum desiccator and residual ammonia and tetrahydrofuran were removed at reduced pressure. The white residue was extracted with chloroform (~500 mL) for 12 h at 25 °C, and 90.5 g of solid was isolated from the chloroform solution. Further extraction of the residue with chloroform for 24 h yielded an additional 24.0 g of solid. The combined, extracted products were then recrystallized from tetrahydrofuran to yield the water-soluble 1,*trans*-3,*trans*-5-triamino-1,3,5-tris(dimethylamino)cyclotriphosphazene (I) (114 g, 83.0%), mp 160–163 °C.

A mass spectrum indicated a molecular weight of 315 (theory for I 315). The infrared spectrum was consistent with the expected structure. Anal. Calcd for $C_6H_{24}N_9P_3$: C, 22.86; H, 7.67; N, 39.99; P, 29.48. Found: C, 23.32; H, 7.81; N, 39.20; P, 29.14. A ^{31}P NMR spectrum in D_2O solvent showed two main peaks at -24.3 ppm (28) and -24.4 ppm (17) (peak areas in parentheses), and this was compatible with the expected trans structure.

Pyrolysis Technique. The pyrolysis reactions were carried out by two different methods. First, pyrolyses were effected in a 200-mL glass bulb equipped with a glass break-seal side arm. Before each reaction, the vessel and the phosphazene were dried in vacuum for 16 h. The vessel was charged with a weighed amount of phosphazene (and in some experiments, a manometrically measured quantity of gaseous ammonia) and was sealed under high vacuum. After 89 h at 310 °C the vessel was opened to the vacuum line and the volatile products were fractionated through U-traps held at -112 and -196 °C. The -112 °C trap retained trimethylamine, while the -196 °C trap contained a mixture of ammonia and trimethylamine. The quantitative composition of the mixture was determined by comparison of the infrared absorbance of the N–H stretching vibration of ammonia (3335 cm^{-1}) in the spectrum of the mixture with standard spectra of pure ammonia. Trimethylamine was identified by vapor pressure measurements, mass spectra, and infrared spectra. The yellow or brown phospham-type residues had very broad infrared absorption bands centered at 3150 (s), 1630 (m), 1540 (m), 1150 (vs), 910 (vs), 835 (vs), and 720 (s) cm^{-1}. The data shown in Table I were obtained by this pyrolysis technique.

In a second method of pyrolysis, rapid thermal decomposition of the aminophosphazenes was accomplished by the heating of a sample of the compound contained in the high-vacuum system using a hand torch. Volatile products were condensed into a liquid nitrogen trap as they formed. Thermal degradation of 3.24 mmol of $[NP(NHCH_3)_2]_3$ gave 11.4 mmol of a mixture of monomethylamine and ammonia. In a similar experiment, incomplete decomposition of 3.33 mmol of *trans*-$[NP(NH_2)(N(CH_3)_2)]_3$ (I) gave 2.42 mmol of dimethylamine and 0.50 mmol of ammonia. The amines were identified by infrared spectroscopy, vapor-phase measurements, and mass spectrometry.

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Registry No. I, 64114-11-0; II, 7142-98-5; III, 1635-63-8; IV, 40101-94-8; V, 974-68-5; 1,*trans*-3,*trans*-5-trichloro-1,3,5-tris(dimethylamino)cyclotriphosphazene, 957-10-8; ammonia, 7664-41-7.

References and Notes

(1) Previous paper in this series: H. R. Allcock, T. J. Fuller, D. P. Mack, K. Matsumura, and K. M. Smeltz, *Macromolecules*, **10**, 824 (1977).
(2) For reviews of this subject see H. R. Allcock, *Chem. Rev.*, **72**, 315 (1972); H. R. Allcock, "Phosphorus-Nitrogen Compounds", Academic Press, New York, N.Y., 1972, Chapter 7.
(3) H. R. Allcock and R. L. Kugel, *Inorg. Chem.*, **5**, 1716 (1966).
(4) H. R. Allcock, W. J. Cook, and D. P. Mack, *Inorg. Chem.*, **11**, 2584 (1972).
(5) H. R. Allcock, *Science*, **193**, 1214 (1976).
(6) L. F. Audrieth and D. B. Sowerby, *Chem. Ind.* (*London*), 748 (1959).
(7) J. Issoire and Co-Van Long, *Bull. Soc. Chim. Fr.*, 2004 (1960).
(8) D. B. Sowerby and L. F. Audrieth, *Chem. Ber.*, **94**, 2670 (1961).
(9) Only 2.5% decomposition in 89 h at 310 °C.
(10) H. Bode and H. Clausen, *Z. Anorg. Chem.*, **258**, 100 (1949).
(11) H. R. Allcock and W. J. Cook, *Macromolecules*, **7**, 284 (1974).
(12) H. R. Allcock, G. Y. Moore, and W. J. Cook, *Macromolecules*, **7**, 571 (1974).
(13) Provided no P–Cl bonds are present.
(14) R. Keat and R. A. Shaw, *J. Chem. Soc.*, 2215, (1965).
(15) G. R. Feistel and T. Moeller, *J. Inorg. Nucl. Chem.*, **29**, 2731 (1967).

Contribution from the Department of Chemistry,
Faculty of Science, Ibaraki University, Mito 310, Japan

Solvent Effects on Rates of Reductions of Some Cobalt(III) Complexes by Iron(II), Vanadium(II), and Chromium(II) in Acidic Aqueous Solutions of *N*,*N*-Dimethylformamide and Alcohols

K. Ohashi,* T. Amano, and K. Yamamoto

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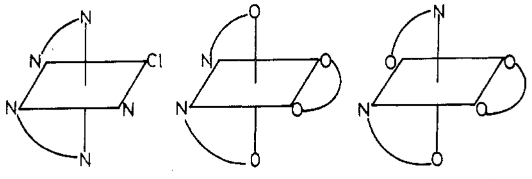
Previous kinetic studies[1,2] of the effect of organic solvents such as *N*,*N*-dimethylformamide ($HCONMe_2$), dimethyl sulfoxide, ethanol, and acetone on the rates of reductions of *cis*-$Co(Cl)(NH_2CH_2CH_2OH)(en)_2^{2+}$ (I) , *cis*(*N*)-Co(ox)-(α-ala)$_2^-$ (II),[3] and *cis*(*N*)-Co(ox)(β-ala)$_2^-$ (II)[3] by iron(II) have shown that the rates of the reductions increased with increase in the mole fraction of organic solvents.



I II

Recently, Watts et al.[4] investigated reductions of $Co(X)(NH_3)_5^{2+}$ ($X = F^-$, Cl^-, and Br^-) by iron(II) in pure *N*,*N*-dimethylformamide, dimethyl sulfoxide, and aqueous solutions of dimethyl sulfoxide. They presented evidence suggesting that the coordination sphere of the iron(II) in the inner-sphere-bridged intermediate changes from octahedral structure in water to tetrahedral structure with the increase in the content of dimethyl sulfoxide in the case of $Co(X)(NH_3)_5^{2+}$ ($X = Cl^-$ and Br^-) and that iron(II) maintains octahedral coordination in the inner-sphere-bridged intermediate for the reduction of $Co(F)(NH_3)_5^{2+}$ by iron(II).

A lot of data about the organic solvent effect on redox reactions should be accumulated to discuss the mechanism of redox reactions in detail. In this work, the kinetic study of reactions of *cis*-$Co(Cl)(NH_2CH_2CH_2OH)(en)_2^{2+}$ and *cis*-(*N*)-Co(ox)(β-ala)$_2^-$ by iron(II), $Co(en)_3^{3+}$, $Co(Cl)(NH_3)_5^{2+}$, and $Co(N_3)(NH_3)_5^{2+}$ by vanadium(II), and $Co(en)_3^{3+}$ by chromium(II) was carried out to obtain further information about the effect of *N*,*N*-dimethylformamide and alcohols such as methanol, ethanol, 2-propanol, and 2-methyl-2-propanol on the reductions of these cobalt(III) complexes.

Furthermore, the effect of ionic strength on the rates of reductions of $Co(en)_3^{3+}$ and $Co(Cl)(NH_3)_5^{2+}$ by vanadium(II) and $Co(en)_3^{3+}$ by chromium(II) in nonaqueous systems was investigated.

Experimental Section

Materials. *cis*(*N*)-K[Co(ox)(β-ala)$_2$],[5] *cis*-$[Co(Cl)(NH_2CH_2CH_2OH)(en)_2]Cl_2$,[6] $[Co(N_3)(NH_3)_5](ClO_4)_2$,[7] $[Co(Cl)(NH_3)_5](ClO_4)_2$,[8] and $[Co(en)_3](ClO_4)_3$,[9] used as the oxidants, were prepared by methods similar to those described in the references cited. The identity and purity of the complexes were confirmed by microanalyses for carbon, hydrogen, and nitrogen and by comparing the molar extinction coefficients at the low-energy absorption maximum with those reported.

The preparation of the iron(II) stock solution and the determinations of the concentrations of the iron(II), hydrogen, and perchlorate ions in this solution were carried out by the method reported in the previous paper.[10] In all cases, the hydrogen and perchlorate ion concentrations of the solution were adjusted by the addition of perchloric acid and sodium perchlorate solutions.

The acidic solution of chromium(III) perchlorate was prepared by the reduction of sodium dichromate in perchloric acid by hydrogen peroxide. Solutions of chromium(II) perchlorate were prepared by the reduction of chromium(III) perchlorate with zinc amalgam. The concentrations of chromium(II) ion and hydrogen ion in chromium(II) solution were determined by the method reported in the literature.[11,12]

The acidic solution of vanadium(IV) perchlorate was prepared by dissolving vanadium metal, 99.99% purity, into excess perchloric acid. Solutions of vanadium(II) perchlorate were obtained by the reduction of vanadium(IV) perchlorate solution with zinc amalgam. The concentrations of vanadium(II) ion and hydrogen ion in vanadium(II) solution were analyzed by a method similar to that described in the reference cited.[13]

N,*N*-Dimethylformamide of spectroscopic grade (Tokyo Kasei) was used without further purification. Methanol, ethanol, 2-propanol, and 2-methyl-2-propanol of reagent grade (Tokyo Kasei) were distilled before use.

Kinetic Measurements. The kinetic measurements of the reductions of *cis*-$Co(Cl)(NH_2CH_2CH_2OH)(en)_2^{2+}$ and *cis*(*N*)-Co(ox)(β-ala)$_2^-$ by iron(II) at below 0.30 mol fraction of methanol were followed spectrophotometrically using a Hitachi EPS-3 type spectrophotometer.

The kinetic measurements of the reductions of $Co(en)_3^{3+}$ by vanadium(II) and chromium(II) were carried out under nitrogen gas atmosphere by a method similar to that for the reduction of *cis*-$Co(Cl)(NH_2CH_2CH_2OH)(en)_2^{2+}$ by iron(II).[1]

The kinetic measurements of reductions of *cis*(*N*)-Co(ox)(β-ala)$_2^-$ by iron(II) above 0.30 mol fraction of methanol and the reduction of $Co(X)(NH_3)_5^{2+}$ ($X = Cl^-$ and N_3^-) by vanadium(II) in aqueous solutions and in aqueous solutions of *N*,*N*-dimethylformamide or alcohols were carried out by the stopped-flow method, using a Hitachi EPS-1 rapid-scan spectrophotometer.

All the kinetic experiments were carried out using a large excess of reductant. Temperatures were kept at 25.0 ± 0.2 °C during the series of experiments.

For all systems the concentration of perchlorate ion of the solution was adjusted by the addition of sodium perchlorate and perchloric acid. The concentration of perchloric acid was maintained over a range of 0.03–0.80 M.

Results and Discussion

The Effect of Organic Solvent on the Reduction Rates. The rate of reduction of cobalt(III) complexes by reductants such as iron(II), vanadium(II), and chromium(II) is first order dependent on the concentrations of reductants and cobalt(III) complexes, respectively, in aqueous solutions of organic solvent. The second-order rate constant of the reduction of *cis*-$Co(Cl)(NH_2CH_2CH_2OH)(en)_2^{2+}$ by iron(II) in aqueous solutions of such alcohols as methanol, ethanol, 2-propanol, and 2-methyl-2-propanol gradually increases with the mole fraction of alcohols up to ca. 0.53 mol fraction of the alcohols (Table I). The rate of reduction increases with the increase in the number of carbon atoms of the alcohols: 2-methyl-2-propanol