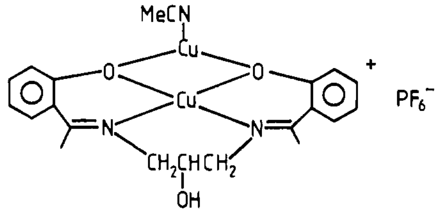
Table IX. Cyclic Voltammetric Data for the Oxidation of Nickel(II) Compounds at the Platinum Electrode[a]

compd	temp, °C	E_p^f, V vs. SCE	E_p^r, V vs. SCE	ΔE_p, mV	i_p^r/i_p^f
3a	20	0.950	0.727	223	0.8
5	−47	1.01	0.47	540	0.9
7a	20	0.745	0.630	115	0.68
7a	−47	0.840	0.450	390	1.19

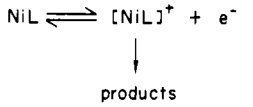
[a] In DMF; supporting electrolyte 0.1 M Et_4NClO_4; scan rate 100 mV s^{-1}. In the case of an oxidation process the superscripts f and r now denote forward (oxidative) and reverse (reductive) scan directions, respectively.

matically as **11**. This species is similar to that proposed by Okawa and Kida[33] for a related compound.



11

Oxidation Processes at the Platinum Electrode. The oxidation of the mononuclear nickel(II) complex **7a** is well-defined (Figure 8). The variation of the oxidation to reduction peak current ratio, with scan rate, for **7a** implies that the product is unstable and that the reaction can be represented by



$$\mathrm{NiL} \rightleftharpoons \underset{\substack{\downarrow \\ \text{products}}}{[\mathrm{NiL}]^+} + e^- \qquad (18)$$

However, the small oxidation current, relative to the one-electron-reduction current, suggests considerable complexity and mechanistic details are unknown. Two oxidation processes are evident for **3a** at room temperature. The data for the first oxidative step are given in Table IX. However, the second oxidation, which occurs at more positive potential, was difficult to reproduce, a factor that may be due to precipitation of products on the electrode surface, as the current rapidly decays to zero in repetitive scanning under conditions of cyclic voltammetry. Two irreversible oxidation steps (0.8 and 1.1 V vs. SCE) are observed for **6** at room temperature while corresponding values of 0.82, 1.04 (**4**) and 1.0, and 1.2 V (**1**) are found at a scan rate of 100 mV s^{-1} for other compounds. In all cases chemical reactions and electrode surface reactions are competing with slow electron-transfer processes. Electrochemically reversible or quasi-reversible oxidations have been reported for a number of mononuclear nickel(II) compounds in acetonitrile.[15,34,35] This solvent may stabilize nickel in oxidation state III but it is not possible to carry out similar experiments in the present case because of the very limited solubility of most compounds in acetonitrile.

Irreversible oxidation of the copper(II) compounds occurs at about 1 V (vs. SCE) at the platinum electrode. Only one oxidation process is observed, and coating of the electrode with electrode-inactive material occurs as in the case of the nickel complexes. The electrochemical oxidation reactions are also irreversible at low temperatures (−60 °C).

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Registry No. **1**, 100230-53-3; **2a**, 100230-54-4; **2b**, 97703-60-1; **3a**, 100230-55-5; **3b**, 97703-56-5; **4**, 100230-56-6; **5**, 100230-57-7; **6**, 100230-58-8; **7a**, 100230-59-9; **7b**, 100230-60-2; **8a**, 100230-61-3; **9**, 100230-62-4; **10**, 100243-61-6; **11**, 100230-64-6; tetrakis(acetonitrile)-copper(I) hexafluorophosphate, 64443-05-6.

Supplementary Material Available: Tables SI and SII, listing electronic absorption spectra and ^{13}C NMR data, respectively, for nickel(II) compounds (2 pages). Ordering information is given on any current masthead page.

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(33) Okawa, H.; Kasempimolporn, V.; Kida, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 647.

(34) Olson, D. C.; Vasilevskis, J. *Inorg. Chem.* **1969**, *8*, 1611.

(35) Bencini, A.; Fabbrizzi, L.; Poggi, A. *Inorg. Chem.* **1981**, *20*, 2544.

(36) See paragraph regarding supplementary material at the end of the paper.

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Acid Decomposition Reactions of Diperoxo(amine)chromium(IV) Complexes

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The acid decomposition reactions of two diperoxo amine complexes of Cr(IV), viz. diperoxoaquo(ethylenediamine)chromium(IV), $Cr(O_2)_2(en)(H_2O)$, and diperoxo(diethylenetriamine)chromium(IV), $Cr(O_2)_2(dien)$, have been investigated at various H^+ concentrations. Three products have been obtained from the acid decomposition at 25–30 °C, and their relative proportions vary as a function of $[H^+]$. The products have been identified to be Cr(VI) (as $H_2Cr_2O_7$), $Cr(H_2O)_6^{3+}$, and $Cr(en)(H_2O)_4^{3+}$ in the case of $Cr(O_2)_2(en)(H_2O)$. The dien derivative gives minor amounts of Cr(VI) as well as $Cr(H_2O)_6^{3+}$ and substantial amounts of $Cr(dienH)(H_2O)_4^{4+}$. Kinetic as well as product analysis data have been rationalized in terms of a reaction scheme involving monoperoxochromium(VI), 6-coordinate chromium(IV), and hydroperoxo radical intermediates. The formation of the hydroperoxo radical intermediate has also been detected by means of scavenging experiments with tetranitromethane. The data have been discussed in terms of a model in which the nuclear reorganizations needed for the conversion of Cr(VI) to octahedral Cr(III) derivatives are important.

Introduction

There has been much current interest in the study of transition-metal complexes in unusual oxidation states,[2–4] particularly in view of their possible roles in biochemical and chemical catalysis.[5,6] Since clinical use of Cr(III) in the control of diabetes

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(2) (a) Jacobi, M.; Meyerstern, D.; Lillie, J. *Inorg. Chem.* **1979**, *18*, 429. (b) Haines, R.; McAuley, A. *Inorg. Chem.* **1980**, *19*, 719.

(3) (a) Nag, K.; Chakravorty; A. *Coord. Chem. Rev.* **1980**, *33*, 87. (b) Korvenvanta, J.; Saarinen, H.; Nasakkala, M. *Inorg. Chem.* **1982**, *21*, 4296. (c) Camenzind, M. J.; Hollander, F. J.; Hill, C. L. *Inorg. Chem.* **1982**, *21*, 4301.

(4) (a) Ullrich, V. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 701. (b) Ferraudi, F.; Muralidharan, S. *Inorg. Chem.* **1981**, *20*, 4267.

0020-1669/86/1325-0915$01.50/0

is being visualized,[7-12] the possible formation of Cr(IV) under physiological conditions and its reaction behavior must also be examined. Studies on the aqueous chemistry of chromium(IV) have been limited. Among the well-characterized examples of chromium(IV) complexes, diperoxoaquo(ethylenediamine)chromium(IV), $Cr(O_2)_2(en)(H_2O)$ (**1**), and diperoxo(diethylenetriamine)chromium(IV), $Cr(O_2)_2(dien)$ (**2**), are of particular interest.[13-16]

The X-ray structure of **1** is known, and the assignment of tetravalency to the metal ion is supported by the O–O bond length and vibrational frequencies corresponding to O_2^{2-} units.[13] The arrangement of ligand atoms in **1** and **2** has been reported to be one of pentagonal-bipyramid geometry in which all four peroxidic oxygens and one of the nitrogen donors of the amine share the corners of a regular pentagon.[13-15] These complexes, therefore, represent an unusual assembly of chromium in an unusual oxidation state with a potentially two-electron-equivalent redox agent, O_2^{2-}. Both Cr(IV) and O_2^{2-} units are capable of reduction as well as oxidation, and only a limited number of studies of these complexes have been reported.[17,18] Therefore, the aqueous chemistry of the diperoxo amine complexes **1** and **2** has now been investigated in detail.

Experimental Section

Materials. The complexes $Cr(O_2)_2(en)(H_2O)$ and $Cr(O_2)_2(dien)$ were prepared and characterized according to standard procedures.[14] The Cr:N ratios were obtained by means of chromate analyses and micro-Kjeldahl determinations. Authentic samples of $Cr(en)(H_2O)_4^{3+}$, 1,2,3-$Cr(dien)(H_2O)_3^{3+}$, and 1,2,6-$Cr(dien)(H_2O)_3^{3+}$ were prepared by using standard methods.[19-21] All other materials used were of reagent grade or better.

Product Analyses. The reaction mixtures (80 mL) for acid decomposition of $Cr(O_2)_2(en)(H_2O)$ and $Cr(O_2)_2(dien)$ at $[Cr(IV)] = (1-3) \times 10^{-3}$ M, $[H^+] = 0.01–0.60$ M, and 25 °C were prepared. The product analysis was carried out by ensuring that all transfers were quantitative. The nonionic products were first obtained by passing the reaction mixtures successively through a Dowex 1-X8 and Dowex 50W-X2 (8 cm × 0.8 cm) columns after onefold dilution of the reaction mixture. The nonionic products were analyzed by means of iodometric titrations. The anionic products were eluted with 1 M HCl from a Dowex 1-X8 column on which they had been absorbed. A yellow anionic product with an electronic spectrum comparable to that of a mixture of Na_2CrO_4 and HCl (1 M) was obtained.

The cationic products of the acid decomposition of $Cr(O_2)_2(en)(H_2O)$ and $Cr(O_2)_2(dien)$ were analyzed after elution from Dowex 50W-X2 columns on which they were first absorbed. Eluting with a mixture of sodium perchlorate and perchloric acid (0.79 M Na^+ and 0.01 M H^+) gave a blue species with absorption maxima at 575 nm (13.8 M^{-1} cm^{-1}) and 408 nm (15.5 M^{-1} cm^{-1}), which compare well with the spectral data of $Cr(H_2O)_6^{3+}$.[22] Further elution with 2.4 M $NaClO_4$ at pH 1.0 gave pink Cr(III) products with absorption maxima at 517 nm (42.2 M^{-1} cm^{-1}) and 387 nm (24.6 M^{-1} cm^{-1}) in the case of $Cr(O_2)_2(en)(H_2O)$ and at 515 nm (46 M^{-1} cm^{-1}) and 385 nm (26.2 M^{-1} cm^{-1}) in the case of decomposition of the $Cr(O_2)_2(dien)$ derivative. Micro-Kjeldahl and chromate analyses of the pink products showed Cr:N ratios of 1:2 and 1:3 (within experimental error) for the en and dien derivatives, respectively. The electronic spectra supported the formulations of $Cr(en)(H_2O)_4^{3+}$ and $Cr(dienH)(H_2O)_4^{4+}$ for the pink products[18,19] of the acid decomposition reactions of $Cr(O_2)_2(en)(H_2O)$ and $Cr(O_2)_2(dien)$, respectively. Quantitative analysis of various products was carried out after ion-exchange separations.

Table I. Distribution of Various Chromium Products Obtained on the Acid Decomposition of Diperoxoaquo(ethylenediamine)chromium(IV) at Various $[H^+]$

$[H^+]$, M	% Cr(VI)	% $Cr(H_2O)_6^{3+}$	% $Cr(en)(H_2O)_4^{3+}$
0.05	60.6	31.3	8.0
0.05[a]	58.6	29.2	10.0
0.10	53.9	32.0	14.8
0.10[b]	50.8	34.3	16.0
0.20	39.0	36.6	16.5
0.20[a]	38.2	41.0	17.9
0.40	22.6	40.0	31.6
0.60	11.8	36.6	42.3

[a] Reaction carried out in the presence of 0.10 M LiBr. [b] Reaction carried out in the presence of 0.50 M CH_3OH.

Search for Radical Intermediates. There is a possibility for the involvement of radical intermediates such as O_2H and OH in our reactions. Therefore, scavenging experiments were carried out by using tetranitromethane (TNM), which reacts with O_2H to produce nitroform with absorption coefficients of 10 200 M^{-1} cm^{-1} at 366 nm and 14 500 M^{-1} cm^{-1} at 350 nm.[23,24] Hydroxyl radical, on the other hand, is known to react with Br^- and CH_3OH to produce Br_2^- and CH_2OH radicals,[25] and the search for O_2H and OH was made.

To do this, equal volumes of TNM solutions (containing 0.25 mL in 250 mL of H_2O) and Cr(IV) diperoxo complexes with $[Cr(IV)] = 10^{-3}$ M were mixed and spectra recorded at $[H^+] = 10^{-5}$ or 0.50 M. When $[H^+] = 0.5$ M, nitroform formation was detected at 356 nm. The decomposition of Cr(IV) diperoxo complexes was carried out after the addition of LiBr (0.1 mol) or CH_3OH (0.5 mL) to a Cr(IV) solution (2.5 mM, 80 mL) containing perchloric acid at $[H^+] = 0.25$ or 0.5 M. Then the final products were analyzed as described in the earlier section.

Kinetic Studies. The kinetic studies of the acid-catalyzed decomposition reactions of $Cr(O_2)_2(en)(H_2O)$ as well as $Cr(O_2)_2(dien)$ were carried out by using an Aminco stopped-flow spectrophotometer at wavelengths 370 and 400 nm, respectively. A pseudo-first-order excess of $[H^+]$ over [Cr(VI)] was employed at $I = 1.5$ M ($LiClO_4$). Pseudo-first-order rate constants did not seem to depend on whether $NaClO_4$ or $LiClO_4$ was used as the noncomplexing electrolyte. The concentration conditions for kinetic investigations were as follows: $[Cr(O_2)_2(en)(H_2O)] = (1-3) \times 10^{-3}$ M, $[H^+] = 0.05–0.75$ M, [LiBr] = 0 or 0.1 M, $I = 1.5$ M ($NaClO_4$), 30 °C; $[Cr(O_2)_2(dien)] = (1-4) \times 10^{-3}$ M, $[H^+] = 0.005$ M, $I = 1.0$ M ($NaClO_4$), 30 °C. In the case of the ethylenediamine derivative, two kinetic steps with $t_{1/2} = 0.1–1.0$ and 0.2–14 s were observed. Since the half-lives were distinctly different from each other at low $[H^+]$, the pseudo-first-order plots of $\log (OD_t - OD_\infty)$ against time "t" were linear to greater than 4 half-lives. The decomposition rate constants, k_d, were obtained by usual methods.[26] However, at $[H^+] = 0.2$ M, the half-lives of the first and second steps differed only by a factor of 5. Therefore, a consecutive reaction treatment was carried out according to standard methods to get k_d.[27-29]

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(5) (a) Groves, J. T.; Nemo, T. E.; Myers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032. (b) Groves, J. T.; McClusky, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 859. (c) Nordblom, G. D.; White, R. C.; Coon, M. J. *Arch. Biochem. Biophys.* **1976**, *175*, 534.

(6) Groves, J. T.; Krishnan, S.; Avaria, G. E.; Nemo, T. E. *Adv. Chem. Ser.* **1980**, *No. 191*, 277.

(7) (a) Mertz, W.; Roginski, E. E. In "Newer Trace Elements in Nutrition"; Mertz, W., Cornatzer, W. E., Eds.; Marcel Dekker: New York, 1971; p 125. (b) Hopkins, L. L.; Mohr, H. E. *Ibid.* p 195.

(8) Underwood, E. J. "Trace Elements in Human and Animal Nutrition"; Academic Press: New York, 1977; p 258.

(9) Mertz, W.; Toepfery, E. N.; Roginski, E. E.; Polansky, M. M. *Fed. Proc., Fed. Am. Soc. Exp. Biol.* **1974**, *33*, 659.

(10) (a) Mertz, W.; Schwarz, K. *Am. J. Physiol.* **1959**, *196*, 614. (b) Mertz, W. *Geochem. Environ.* **1974**, *35*, 1.

(11) Rollinson, C. L.; Rosenbloom, E. W. "Coordination Chemistry"; Kirschner, S., Ed.; Plenum Press: New York, 1969; p 108.

(12) (a) Mertz, W. *Physiol. Rev.* **1969**, *49*, 165. (b) Mertz, W.; Toepfrey, E. W.; Roginski, E. L.; Polansky, M. M. *Fed. Proc., Fed. Am. Soc. Exp. Biol.* **1974**, *33*, 11.

(13) Stomberg, R. *Nature (London)* **1965**, *207*, 76.

(14) Garner, C. S.; House, D. A. *Inorg. Chem.* **1966**, *5*, 840.

(15) (a) Hughes, R. G.; Garner, C. S. *Inorg. Chem.* **1968**, *7*, 74. (b) House, D. A.; Hughes, R. G.; Garner, C. S. *Inorg. Chem.* **1967**, *6*, 1077.

(16) House, D. A.; Garner, C. S. *Nature (London)* **1965**, *208*, 776.

(17) Sriram, M.; Ramasami, T.; Ramaswamy, D. *Inorg. Chim. Acta* **1979**, *36*, L433.

(18) Garner, C. S.; House, D. A. *Transition Met. Chem. (N.Y.)* **1970**, *6*, 59 and references therein.

(19) (a) Childers, R. F.; Vanderzyl, K. G.; House, D. A.; Hughes, R. G.; Garner, C. S. *Inorg. Chem.* **1968**, *7*, 749. (b) *Ibid.* **1968**, *7*, 2678.

(20) Caldwell, S. H.; House, D. A. *J. Inorg. Nucl. Chem.* **1969**, *31*, 811.

(21) House, D. A.; Garner, C. S. *Inorg. Nucl. Chem. Lett.* **1965**, *1*, 137.

(22) Earley, J. E.; Cannon, R. D. *Transition Met. Chem.* **1965**, *1*, 34.

(23) Rabani, J.; Mulac, W. A.; Matheson, M. S. *J. Phys. Chem.* **1965**, *69*, 53.

(24) Matheson, M. S.; Dorfman, L. M. "Pulse Radiolysis"; American Chemical Society: Washington, DC, 1969; pp 71, 81.

(25) Gordon, S.; Hart, E. J.; Matheson, M. S.; Rabani, J.; Thomas, J. K. *Discuss. Faraday Soc.* **1963**, 193.

(26) (a) Harmer, M. A.; Richens, D. T.; Soares, A. B.; Thronton, A. T.; Sykes, A. G. *Inorg. Chem.* **1981**, *20*, 4155. (b) Ramasami, T.; Sykes, A. G. *Inorg. Chem.* **1976**, *15*, 2885.

(27) Capellos, C.; Bielski, B. H. J. "Kinetic Systems"; Interscience: New York, 1972; p 46.

(28) Ranganathan, H.; Ramasami, T.; Ranganathan, C. K.; Ramaswamy, D.; Santappa, M. *Int. J. Chem. Kinet.* **1982**, *14*, 161.

(29) Marty, W.; Espenson, J. H. *Inorg. Chem.* **1979**, *18*, 1246.

The pseudo-first-order rate constants, k_d, were measured as a function of [H$^+$] and [LiBr] at $I = 1.5$ M. In the case of the dien complex, only one kinetic step was observed and it had a $t_{1/2}$ of 0.8–40 s. The pseudo-first-order rate constants, k'_d, were measured at various [H$^+$] concentrations at $I = 1.0$ M (LiClO$_4$) and 30 °C.

Treatment of Kinetic Data. The kinetic data obtained under various conditions were analyzed for their dependence on [H$^+$] by using an IBM 370 computer and the Los Alamos program and suitable subroutines written by Moore et al.,[30] which were implemented by Espenson and co-workers.[31]

Results and Interpretation

Although it had been reported previously that only Cr(en)(H$_2$O)$_4^{3+}$ was formed when Cr(O$_2$)$_2$(en)(H$_2$O) was heated at 40 °C under acidic conditions,[14] our spectrophotometric and ion-exchange studies revealed that at 25 °C, apart from Cr(en)(H$_2$O)$_4^{3+}$, a Cr(VI) product with an intense absorption at 360 nm was also formed. The relative proportions of the Cr(III) and Cr(VI) products varied with [H$^+$]. With Cr(O$_2$)$_2$(dien), only at very low [H$^+$], viz. 0.01 M, a charge-transfer band was observed and the predominant products were Cr(III) derivatives. The detailed product analyses of the reactions of Cr(O$_2$)$_2$(en)(H$_2$O) and Cr(O$_2$)$_2$(dien) were carried out by using a number of ion-exchange separations of products. The products of the acid decomposition of Cr(O$_2$)$_2$(en)(H$_2$O) at [H$^+$] ≤ 0.6 M were found to be Cr(VI), Cr(H$_2$O)$_6^{3+}$, and Cr(en)(H$_2$O)$_4^{3+}$, on the basis of reducibility, redox equivalence, N:Cr ratios, charge behavior, and electronic spectra. When [H$^+$] > 0.7 M, the decomposition of Cr(O$_2$)$_2$(en)(H$_2$O) yielded also a brown product (in <2% yield) that slowly underwent further decomposition to pink species. The chemical nature of this product with an apparently high charge could not be established unambiguously due to its low yield and poor stability.

The quantitative analyses of the amounts of the three major products formed on the acid decomposition of Cr(O$_2$)$_2$(en)(H$_2$O) as a function of [H$^+$] gave the data listed in Table I. It is evident from Table I that as the [H$^+$] increased, the amount of Cr(en)(H$_2$O)$_4^{3+}$ formed increased and the Cr(VI) proportion decreased. The amount of Cr(H$_2$O)$_6^{3+}$ was [H$^+$]-independent. The initial reaction of [H$^+$] with Cr(O$_2$)$_2$(en)(H$_2$O) may be easily inferred to be (most likely) one of protonation of O$_2^{2-}$ units by analogy to reactions of V(O$_2$)$_2$O(C$_2$O$_4$)[32] complexes. The internal redox in the protonated derivative may well generate a hydroperoxide radical as in eq 1 that may later decompose to O$_2$ and H$_2$O$_2$ as in eq 2.

$$\mathrm{Cr(O_2)(O_2H)(en)(H_2O)^+} \xrightarrow{2\mathrm{H^+},\ 3\mathrm{H_2O}} \mathrm{Cr(en)(H_2O)_4^{3+} + O_2H + H_2O_2} \quad (1)$$

$$\mathrm{2O_2H \rightarrow O_2 + H_2O_2} \quad (2)$$

The sequence of reactions predicts not only the formation of O$_2$H but also the ratio of O$_2$H:Cr(en)(H$_2$O)$_4^{3+}$ as 1:1. Indeed the experiments with tetranitromethane indicated the formation of nitroform, which is the expected product of the O$_2$H reaction according to eq 3.[23,24] Although qualitative evidence for O$_2$H

$$\mathrm{O_2H + C(NO_2)_4 \rightarrow C(NO_2)_3^- + H^+ + NO_2 + O_2} \quad (3)$$

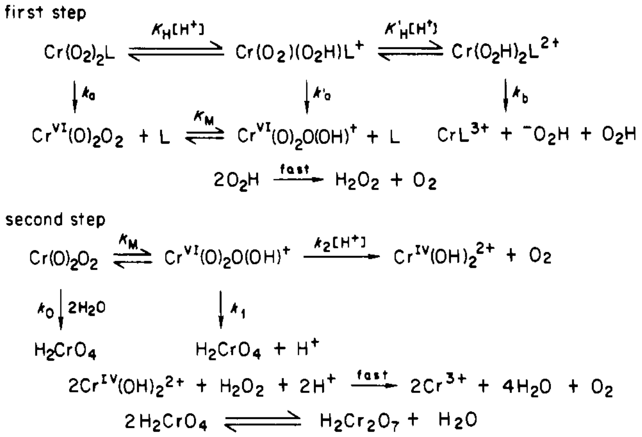
was obtained unambiguously by means of a number of blank experiments, the quantitative stoichiometry of 1 mol of ·O$_2$H/mol of Cr(en)(H$_2$O)$^{3+}$ could not be established, possibly due to the competition of (2) and (3). However, hydroxyl radicals could not be detected even after many scavenging experiments for OH using LiBr and methanol. Oxygen gas formation was, nevertheless, detected.[33] When the cationic and anionic products were removed from the reaction mixture as rapidly as possible (<2 min) and the eluate was deaerated, the nonionic product analyzed for H$_2$O$_2$.

Table II. Distribution of Products Obtained on the Acid Decomposition of Diperoxo(diethylenetriamine)chromium(IV)

[H$^+$], M	% Cr(VI)	% Cr(H$_2$O)$_6^{3+}$	% Cr(III) dien complex[a]
0.05	7.1	15.4	78.8
0.1	1.4	15.4	84.8
0.2	1.5	15.5	82.6
0.3	1.3	15.4	83.2
0.5	1.7	15.6	84.8

[a] Identified later to be Cr(dienH)(H$_2$O)$_4^{4+}$.

Scheme I. General Reaction Scheme for Acid Decomposition of Cr(IV) Diperoxo Amine Complexes



Qualitative detection of H$_2$O$_2$ was made by the formation of reddish brown Ti(IV) peroxo complexes. Iodometric determinations revealed the formation of 0.56 mol of H$_2$O$_2$/mol of Cr(IV) at [H$^+$] = 0.05 M, where acid-catalyzed decomposition to Cr(en)(H$_2$O)$_4^{3+}$ was minimum. Similar product analysis experiments were carried out also for the decomposition reaction of Cr(O$_2$)$_2$(dien).

The main feature of Cr(O$_2$)$_2$(dien) reaction as contrasted to that of Cr(O$_2$)$_2$(en)(H$_2$O) is that only minor amounts of Cr(H$_2$O)$_6^{3+}$ and Cr(VI) products were formed at [H$^+$] = 0.05–0.5 M, as seen from the data listed in Table II. The pink product formed (and isolated by means of ion-exchange separations) had electronic spectral data that resembled those of Cr(dienH)(H$_2$O)$_4^{4+}$ rather than those of any other related Cr(III) dien complexes, as shown in Table III. As in the case of Cr(O$_2$)$_2$(en)(H$_2$O), the formation of H$_2$O$_2$, O$_2$H, and O$_2$ were also detected in the reaction mixtures of the acid decomposition of Cr(O$_2$)$_2$(dien).

Although there were several chromium- as well as oxygen-derived products, the kinetic studies on the acid decompositions of Cr(O$_2$)$_2$(en)(H$_2$O) and Cr(O$_2$)$_2$(dien) were relatively simple. There were two kinetic stages for the acid decomposition of Cr(O$_2$)$_2$(en)(H$_2$O), and the observed pseudo-first-order rates for the first and second stages were denoted as k_d and k_s, respectively. The observed rates, k_d and k_s, are listed in Table IV. The experimental data for both stages may be conveniently fitted to the rate law given in eq 4. In the case of the Cr(O$_2$)$_2$(dien)

$$k_d \text{ or } k_s = A + B[\mathrm{H^+}] + C[\mathrm{H^+}]^2 \quad (4)$$

derivatives, the decomposition in the [H$^+$] region 0.1–0.5 M proceeded in single-stage kinetics and secondary pathways were negligible. The rates measured for the decomposition of the Cr(O$_2$)$_2$(dien) derivative, k'_d, are given in Table V and may be fitted to the rate law given in eq 5.

$$k'_d = \frac{R + S[\mathrm{H^+}] + T[\mathrm{H^+}]^2}{1 + Q[\mathrm{H^+}]} \quad (5)$$

The overall product analyses and kinetic data on the acid decomposition reactions of Cr(IV) diperoxo complexes investigated may be rationalized in terms of a general reaction scheme (Scheme

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(30) Moore, R. H.; Zeigler, R. K. Report No. LA 2367 plus Addenda; Los Alamos Scientific Laboratory: Low Alamos, NM, 1959.

(31) We thank Prof. James H. Espenson for help in the computational treatment of data.

(32) Quititzsch, U.; Weighardt, K. *Inorg. Chem.* **1979**, *18*, 869.

(33) Duplicate measurements of O$_2$ released using gasometric methods revealed that O$_2$ release was approximately 1.6–1.8 times [CrL^{3+}] + [Cr(H$_2$O)$_6^{3+}$] type species.

Table III. Electronic Spectral Data on Various Aquo(diethylenetriamine)chromium(III) Complexes

complex	λ_{max}, nm	ϵ_{max}, $M^{-1}\ cm^{-1}$	λ_{max}, nm	ϵ_{max}, $M^{-1}\ cm^{-1}$	ref
1,2,3-$Cr(dien)(H_2O)_3^{3+}$	375	32.2	510	67	20
1,2,6-$Cr(dien)(H_2O)_3^{3+}$[a]	390	45.4	495	89	20
$Cr(dienH)(H_2O)_4^{4+}$	387	30.0	521	46	18
$Cr(dienH)(H_2O)_4^{4+}$[b]	385	26.2	520	46.7	this work
$Cr(dienH)_2(H_2O)_5^{5+}$	397	23.0	550	23	18

[a] In 1.0 M $HClO_4$. [b] Obtained from the acid decomposition of $Cr(O_2)_2(dien)$.

Table IV. Acid Decomposition Rates for the First Step, k_d, and for the Second Step, k_s, in the Reaction of $Cr(O_2)_2(en)(H_2O)$[a]

10^3[Cr(IV)], M	[H^+], M	k_d,[b] s^{-1}	k_s,[b] s^{-1}
0.17	0.005		0.017
0.17	0.01		0.023
0.18	0.02		0.04
0.18	0.05	0.73	0.14
0.18	0.10	1.31	0.29
0.16	0.175	1.71	
0.18	0.20	2.07	0.51
0.16	0.25	2.60	
0.18	0.30	3.3	0.64
0.16	0.40	4.05	0.80
0.16	0.50	5.30	0.91
0.18	0.60	6.70	
0.18	0.70	7.0	
0.16	0.75	8.1	

[a] Conditions: λ = 370 nm; I = 1.50 M ($NaClO_4$); 30 °C. [b] Average of four determinations.

Table V. Acid Decomposition Rates, k'_d, for the Reactions of $Cr(O_2)_2(dien)$[a]

10^3[Cr(IV)], M	[H^+], M	k'_d,[b] s^{-1}	10^3[Cr(IV)], M	[H^+], M	k'_d,[b] s^{-1}
0.17	0.005	0.017	0.17	0.20	0.51
0.17	0.01	0.023	0.17	0.30	0.14
0.18	0.02	0.04	0.18	0.40	0.80
0.18	0.05	0.14	0.18	0.50	0.91
0.18	0.10	0.29			

[a] Conditions: λ = 400 nm; 30 °C. [b] Average of four determinations.

I, with water ligands omitted). This reaction scheme predicts 1 mol of O_2H/mol of CrL^{3+} and H_2O_2 amounts varying with [H^+] as in eq 6. At [H^+] = 0.05 M, from eq 6 and data given in Table

$$[H_2O_2] = 1.5[CrL^{3+}] + [Cr(VI)] - 0.5[Cr^{3+}] \qquad (6)$$

I, 0.59 mol of H_2O_2/mol of $Cr(O_2)_2(en)(H_2O)$ would be expected according to Scheme I. Indeed the experimental value of H_2O_2 detected per mole of [Cr(IV)], viz. 0.56 mol of H_2O_2/mol of Cr(IV), is in satisfactory agreement with the calculated values. The proposed scheme further implies that the Cr(III) amine complexes and monoperoxo derivatives formulated as $Cr(O_2)(O)_2$ are formed as the primary products in the first step. The formation of monoperoxo complexes like $Cr^{VI}(O_2)(O)_2$ has been visualized in earlier studies in the reactions of Cr(VI) and H_2O_2 also.[34] Although a hexavalent oxidation state has been assigned to the monoperoxo complexes visualized, in complexes such as the ones with which we deal in this study, such oxidation state descriptions must be considered only qualitatively.

According to Scheme I, the observed rate k_d for the first stage is expressed by the rate law (7). The observed rate laws of the

$$k_d = \frac{k_a + k'_a K_H[H^+] + k_b K_H K'_H[H^+]^2}{1 + K_H[H^+] + K_H K'_H[H^+]^2} \qquad (7)$$

forms (5) and (4) are derived easily from (7) when $1 + K_H[H^+] + K_H K'_H[H^+]^2 \simeq 1$ and $1 + K_H[H^+] + K_H K'_H[H^+]^2 \simeq 1 + K_H[H^+]$, respectively, which describe the reactions of $Cr(O_2)_2(en)(H_2O)$ and $Cr(O_2)_2(dien)$ satisfactorily. Since Scheme I assumes parallel first-order reactions in the first stage, the product

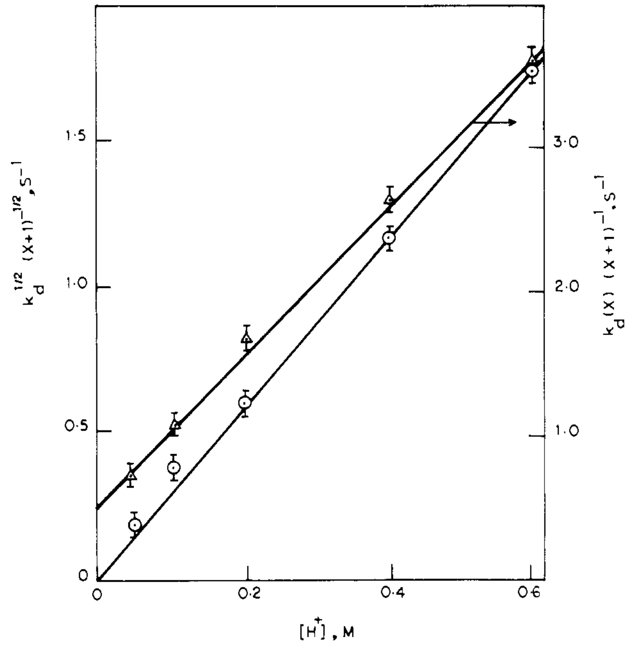

Figure 1. [H^+] dependence of first-stage decomposition rates and products distribution showing the validity of Scheme I for $Cr(O_2)_2(en)(H_2O)$.

ratios for the $Cr(O_2)_2(en)(H_2O)$ reaction must also be reconciled with the rate law (8), if Scheme I is applicable. The product ratios

$$k_d = k_a + k'_a K_H[H^+] + k_b K_H K'_H[H^+]^2 \qquad (8)$$

must be related to (8) as in (9). With $\{[CrO_4^{2-}] + [Cr^{3+}]\}\cdot$

$$\frac{k_a + k'_a K_H[H^+]}{k_b K_H K'_H[H^+]^2} = \frac{[Cr^{VI}\ \text{monoperoxo complex}]}{[CrL^{3+}]} = \frac{[CrO_4^{2-}] + [Cr^{3+}]}{[CrL^{3+}]} \qquad (9)$$

$[CrL^{3+}]^{-1}$ denoted as X, it may be shown that the assumptions made in Scheme I predict linear plots of $k_d(X)(X+1)^{-1}$ as well as $(k_d)^{1/2}(X+1)^{-1/2}$ against [H^+]. Experimentally linear relations for the first stage are observed for $Cr(O_2)_2(en)(H_2O)$, as seen in Figure 1. However, the validity of Scheme I has to be further examined with respect to the product ratios in the second stage also. It is evident from Scheme I that the products (Cr^{3+} and H_2CrO_4 or Cr(VI) in the form of $H_2Cr_2O_7$) are again formed as decomposition products of the monoperoxo complex $Cr(O_2)(O)_2$ in parallel first-order reactions. The observed rate for the second stage, k_s, is given by the rate law (10), when $1 + K_M[H^+] \simeq 1$.

$$k_s = k_0 + k_1 K_M[H^+] + k_2 K_M[H^+]^2 \qquad (10)$$

Similar to the case in the first stage, it may be shown that the product ratios $CrO_4^{2-}:Cr^{3+} = Y$ are also related to first-order rates, k_s, and that linear plots of $Y(k_s)(Y+1)^{-1}$ and $(k_s)^{1/2}\ (Y+1)^{-1/2}$ against [H^+] are predicted by Scheme I. The plots shown in Figure 2 support the consistency of Scheme I with the experimental data. In the case of $Cr(O_2)_2(dien)$ also, the experimental data fitted Scheme I although, as contrasted to $Cr(O_2)_2(en)(H_2O)$, there was only one slow kinetic stage giving k'_d, which is easily fitted to the rate law (11), where k_a, k'_a, k_b, K_H, and K'_H may

$$k'_d = \frac{k_a + k'_a K_H[H^+] + k_b K_H K'_H[H^+]^2}{1 + K_H[H^+]} \qquad (11)$$

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[34] Flood, P.; Lewis, T. J.; Richards, D. H. *J. Chem. Soc.* **1963**, 2446.

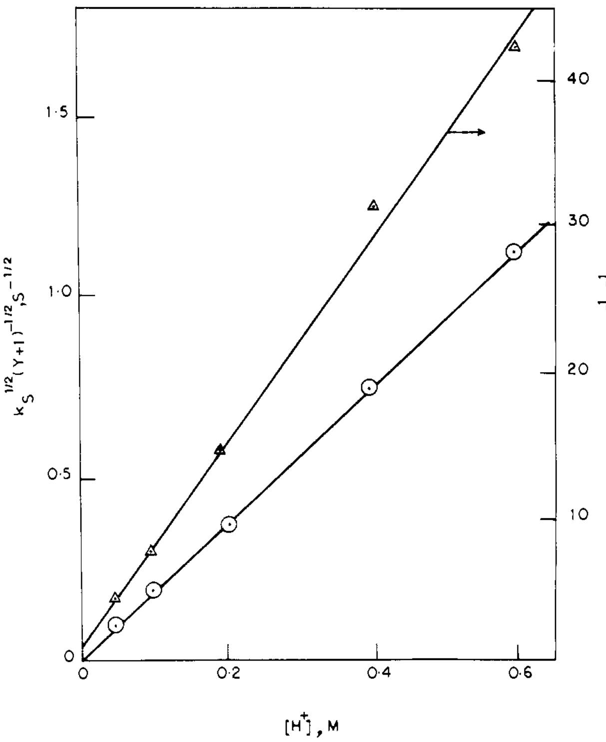


Figure 2. $[H^+]$ dependence of second-stage decomposition rates and product distribution showing the validity of Scheme I for $Cr(O_2)_2(en)(H_2O)$.

Table VI. Kinetic Parameters for the Acid Decomposition Reactions of Cr(IV) Diperoxo Amine Complexes $Cr(O_2)_2L$ at 30 °C with Aquo Ligands Omitted and L = En or Dien

	amine ligand (L)	
parameter	en[a]	dien[b]
$10k_a$, s^{-1}	3.9 ± 0.3	0.018 ± 0.003
k_aK_H, M^{-1} s^{-1}	4.9 ± 0.6	2.28 ± 0.25
$k_bK_HK'_H$, M^{-2} s^{-1}	10.2 ± 1.8	0.35 ± 0.1
10^2k_0, s^{-1}	1.2 ± 0.3	
k_1K_M, M^{-1} s^{-1}	0.69 ± 0.3	
k_2K_M, M^{-2} s^{-1}[c]	3.9 ± 0.4	
K_H, M^{-1}	(0.01)	0.32 ± 0.10

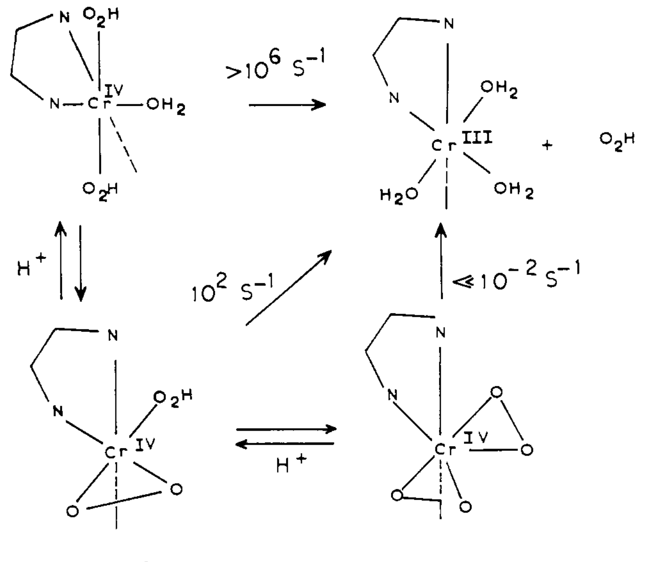
[a] I = 1.50 M ($NaClO_4$). [b] I = 1.00 M ($NaClO_4$). [c] k_2 has second-order rate constant units by definition.

have very different values compared to those for $Cr(O_2)_2(en)(H_2O)$. The complete analyses of the kinetic data using an IBM 370 computer and suitable programs gave the values of k_a, k'_a, K_H, $k_bK_HK'_H$, K_0, k_1K_M, and k_2K_M. In the case of $Cr(O_2)_2(dien)$, K_H could also be obtained through the computation of kinetic data. The various kinetic parameters obtained are listed in Table VI.

Discussion

It is evident from the data listed in Table VI that the ethylenediamine derivative underwent decomposition more rapidly at low $[H^+]$, giving Cr(VI)-derived products. The dien derivative with its higher protonation constant and relative ratios of k_a, k'_a, and k_b seems to undergo decomposition to the Cr(III) aquo amine complex $Cr(dienH)(H_2O)_4^{4+}$ preferentially. Although the protonation behavior of the peroxide units in the vanadium(V) peroxo complexes has been reported previously,[32] the site and effects of protonation in our complexes require further comment. The Cr(IV) diperoxo complexes have two potential protonation sites, viz. peroxide units and amine ligands. It is evident from Table VI that the redox behavior of the complex is related to acid–base equilibria associated with Cr(IV) diperoxo derivatives. It is already established that the redox couples associated with the O_2^{2-} anion are all $[H^+]$-dependent and that the anion is so basic that it exists as HO_2^- even in strongly alkaline solutions.[35] In other words, coordinated O_2^{2-} units may be more basic than coordinated amines and may seem more likely sites of protonation.

Scheme II. Relative Rates of Decomposition of Cr(IV) in Various Geometries to Cr(III) Amine Complexes



The protonation at the O_2^{2-} units would render the dianion unidentate, enabling the Cr(IV) reactants to resemble octahedral Cr(III) products more closely. Since the bite angle and interdonor distances of chelated O_2^{2-} units in the Cr(IV) derivatives are expected to be much smaller than those needed for an octahedral Cr(III) derivative, it is not surprising that the diprotonated derivatives undergo ready decomposition to Cr(III) amine complexes. It is true that K_H could be estimated more precisely in the case of the $Cr(O_2)_2(dien)$ derivative alone as in Table VI and K_H has a higher value for the dien derivative compared to that of the $Cr(O_2)_2(en)(H_2O)$ complex. The higher K_H value for $Cr(O_2)_2(dien)$ may be consistent with the greater electron density at Cr(IV) resulting from the larger field strength of the dien ligands compared to ethylenediamine. The value of 0.01 is an upper limit obtained by fitting the kinetic data for $Cr(O_2)_2(en)(H_2O)$ derivative to rate law 11. Since no noticeable curvature toward the $[H^+]$ axis was observed up to $[H^+]$ = 0.7 M when k_d was plotted against $[H^+]$ in the case of $Cr(O_2)_2(en)(H_2O)$ decomposition, K'_H must have a value equal to or much smaller than 0.01 M estimated for K_H. Therefore, by employment of these estimated values of K_H and K'_H, lower limits for k'_a and k_b may be obtained. The direct decomposition pathways to Cr(III) aquo amine complexes from unprotonated and monoprotonated derivatives must be at least 1 order of magnitude slower than k_a and k'_a, respectively, to be consistent with the data shown in Figure 1. Therefore, the relative rates of decomposition of Cr(IV) diperoxo derivatives to Cr(III) aquo amine complexes in the un-, mono-, and diprotonated forms may be represented as in Scheme II. The protonation of O_2^{2-} and monodentate binding of ^-O_2H would give rise to a more favorable octahedral disposition of ligands, thereby lowering the reorganizational barriers for the conversion into octahedral Cr(III) amine complexes. Therefore, apart from the driving force changes and the potentials of associated redox couples with $[H^+]$, the intrinsic barriers for the conversion of Cr(IV) to Cr(III) also would be influenced by the protonation of O_2^{2-} units. It is interesting that the $Cr(O_2)_2(dien)$ derivative yields $Cr(dienH)(H_2O)_4^{4+}$ rather than 1,2,3,- or 1,2,6-$Cr(dien)(H_2O)_3^{3+}$ as products. Detailed discussions on the nature of six-coordinate Cr(IV) intermediates would have been possible if 1,2,6-$Cr^{III}(dien)(H_2O)_3^{3+}$ did not undergo facile decomposition to $Cr(dienH)(H_2O)_4^{4+}$ as reported earlier.[36]

The results of this study emphasize the importance of reorganization of geometry in the conversion of Cr(IV) to other chromium oxidation states. Hence one of the possible methods

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(35) Evans, M.; Uri, N. *Trans. Faraday Soc.* **1949**, 224.

(36) House, D. A. *Inorg. Nucl. Chem. Lett.* **1967**, *3*, 367.

of stabilizing Cr(IV) without decomposition to Cr(III) or Cr(V) may well be one of placing the metal ion in a coordination geometry and environment that are uncommon or constrained with tri- and pentavalent states. Recently, a Cr(IV) porphyrin derivative has been prepared and characterized.[37] Further work in the area of stabilization of uncommon oxidation states by way of manipulation of reorganizational barriers is in progress.[38]

Registry No. $Cr(O_2)_2(en)(H_2O)$, 17192-14-2; $Cr(O_2)_2(dien)$, 59419-71-5; $Cr(en)(H_2O)_4^{3+}$, 16702-61-7; $Cr(dienH)(H_2O)_4^{4+}$, 24249-47-6; $Cr(H_2O)_6^{3+}$, 14873-01-9; $H_2Cr_2O_7$, 13530-68-2.

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(37) Groves, J. T.; Kruper, W. J.; Haushalter, R. C.; Butler, W. M. *Inorg. Chem.* **1982**, *21*, 1363.

(38) Nair, B. U.; Ramasami, T.; Ramaswamy, D. *Inorg. Chem.* **1986**, *25*, 51, and references therein; also unpublished work.

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Reactions of Pentachloro- and Pentafluoro(triphenylphosphazenyl)cyclotriphosphazenes with Sodium Methoxide. Mechanistic Aspects and Their Implications for Nucleophilic Displacement at a Tetrahedral Phosphorus(V) Center[1]

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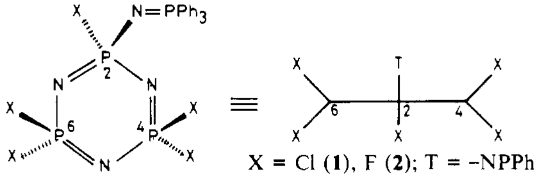
Reactions of $N_3P_3(NPPh_3)X_5$ [X = Cl (**1**), F (**2**)] with sodium methoxide afford the derivatives $N_3P_3(NPPh_3)(OCH_3)_nX_{5-n}$ (n = 1-5; X = Cl, F) (**3**–**20**), whose structures have been elucidated by NMR (^{1}H, ^{31}P, and ^{19}F) spectroscopy. The successive replacement of chlorine from **1** yields geometrical isomers in unequal proportions whereas the substitution of fluorine from **2** gives geometrical isomers in roughly equal proportions. The chlorine at the $\equiv P(NPPh_3)Cl$ center is easily replaced whereas the fluorine at the $\equiv P(NPPh_3)F$ site is not replaced until the last stage. These differences are rationalized in terms of a changeover from an $S_N2(P)$ to an $S_N1(P)$ mechanism for the methoxylation of **1** at later stages of substitution and an $S_N2(P)$ mechanism persisting throughout for the fluoro system. Attack of the methoxide in the plane of the phosphazene ring is postulated to explain the stereochemical course found for the reaction of **2**.

Numerous investigations on the nucleophilic displacement reactions of halogenocyclophosphazenes have been primarily concerned with an understanding of the behavior of the attacking nucleophile.[2-4] Despite these extensive studies, a comprehensive model to explain all the findings has not yet emerged. The effects of (a) the substituent already present on the ring, (b) the leaving group, and (c) the solvent have not been assessed in any detail to rationalize the "regio- and stereoselectivity" observed in these reactions. Any progress in this area should have wider ramifications for understanding the stereochemistry of displacement at a tetracoordinate P(V) center. We have chosen the pentachloro- and pentafluoro(triphenylphosphazenyl)cyclotriphosphazenes, $N_3P_3(NPPh_3)X_5$ [X = Cl (**1**), F (**2**)], as substrates to study the differences in the mechanisms of displacement reactions at P–Cl and P–F centers.[5] Both **1** and **2** are high-melting solids and can be handled more conveniently than $N_3P_3Cl_6$ and $N_3P_3F_6$, the latter of which is very volatile. Furthermore, the $-NPPh_3$ group exerts a geminal-directing influence in the reactions of **1** with secondary amines[6] and hence it would be of interest to study the effect with other nucleophiles. The choice of the substrates is also dictated by the fact that the shielding effect of the $-NPPh_3$ group on the protons of the cis substituent[6] and the magnitude of phosphorus-phosphorus coupling in the ^{31}P NMR spectra facilitate structural assignments to geometrical and positional isomers.



X = Cl (**1**), F (**2**); T = $-NPPh_3$

In this paper, we report the results of a detailed investigation of the reactions of **1** and **2** with sodium methoxide.[7] This investigation constitutes the first systematic study of the reaction of a fluorocyclotriphosphazene with an alkoxide. The results are correlated with those observed in the nucleophilic displacement reactions at a tetrahedral P(V) center in other systems.

Results and Discussion

Methoxylation of **1** or **2** can lead to 19 substitution products of the type $N_3P_3(NPPh_3)(OCH_3)_nX_{5-n}$ [X = Cl, F; n = 1 and 4 (three isomers each), 2 and 3 (six isomers each), and 5]. The structural elucidation of the derivatives obtained in the present study by NMR spectroscopy is based upon the following criteria: (a) ^{1}H NMR (i) the number of methoxy environments and the presence or absence of "virtual coupling",[8] (ii) the magnitude of ^3J(P–H), and (iii) the relative chemical shifts of the cis and trans (with respect to the $-NPPh_3$ substituent) $-OCH_3$ protons; (b) ^{31}P NMR (i) the number of phosphorus environments, (ii) the chemical shift values, and (iii) the magnitude of ^2J(P–P); (c) ^{19}F

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(1) Studies of Phosphazenes. 28. Part 27: Kumara Swamy, K. C.; Ramabrahmam, P.; Krishnamurthy, S. S. *Synth. React. Inorg. Met.-Org. Chem.* **1985**, *15*, 1023.

(2) (a) Karthikeyan, S.; Krishnamurthy, S. S. *Z. Anorg. Allg. Chem.* **1984**, *513*, 231. (b) Evans, T. L.; Allcock, H. R. *Inorg Chem.* **1979**, *18*, 2342. (c) Ramachandran, K.; Allen, C. W. *Inorg. Chem.* **1983**, *22*, 1445. (d) Van der Huizen, A. A.; Jekel, A. P.; Rusch, J.; van de Grampel, J. C. *Recl. Trav. Chim. Pays-Bas* **1981**, *100*, 343.

(3) (a) Krishnamurthy, S. S.; Sundaram, P. M; Woods, M. *Inorg. Chem.* **1982**, *21*, 406. (b) Dhathathreyan, K. S.; Krishnamurthy, S. S.; Woods, M. *J. Chem. Soc., Dalton Trans.* **1982**, 2151.

(4) For a review, see: Krishnamurthy, S. S.; Sau, A. C.; Woods, M. *Adv. Inorg. Chem. Radiochem.* **1978**, *21*, 41.

(5) For a similar study with metallocenyl anions see: Allcock, H. R.; Lavin, K. D.; Riding, G. H; Suszko, P. R.; Whittle, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 2337.

(6) (a) Krishnamurthy, S. S.; Ramabrahmam, P.; Vasudeva Murthy, A. R.; Shaw, R. A.; Woods, M. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 215. (b) Biddlestone, M.; Shaw, R. A. *J. Chem. Soc., Dalton Trans.* **1973**, 2740. (c) Nabi, S. N.; Biddlestone, M.; Shaw, R. A. *J. Chem. Soc., Dalton Trans.* **1975**, 2634. (d) Ramabrahmam, P.; Krishnamurthy, S. S.; Vasudeva Murthy, A. R.; Shaw, R. A.; Woods, M. *Z. Anorg. Allg. Chem.* **1985**, *522*, 226.

(7) A part of this work has appeared as a communication. See: Kumara Swamy, K. C.; Krishnamurthy, S. S. *Phosphorus Sulfur* **1983**, *18*, 241.

(8) Finer, E. G.; Harris, R. K.; Bond, M. R.; Keat, R.; Shaw, R. A. *J. Mol. Spectrosc.* **1970**, *33*, 72.

(9) Biddlestone, M.; Keat, R.; Rose, H.; Rycroft, D. S.; Shaw, R. A. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1976**, *B31*, 1001.

0020-1669/86/1325-0920$01.50/0