Reagents. Cobalt octacarbonyl, $Co_2(CO)_8$, was used as obtained from Strem Chemicals, Danvers, Mass. When not in use it was stored at −79 °C under a nitrogen atmosphere.

***n*-Hexane**, purchased from Fisher Scientific, Medford, Mass., was distilled from lithium aluminum hydride and purified by fractional condensation through traps at −45, −63, and −196 °C until the material retained at −63 °C exhibited a vapor pressure of 45 mm at 0 °C.

Iodine, from Merck and Co., Inc., Rahway, N.J., was vacuum sublimed before use.

Methylene chloride, CH_2Cl_2, from Mallinckrodt Chemicals, St. Louis, Mo., was dried by distillation from phosphorus pentoxide and purified by fractional condensation through traps at −63, −98, and −196 °C. The fraction retained at −98 °C which exhibited a vapor pressure of 40 mm at −23 °C was assumed to be pure CH_2Cl_2.

Pentacarbonylphosphinochromium, $H_3PCr(CO)_5$, was prepared by the method of Klabunde et al.[4] The physical properties agreed with those in the literature.[4,5]

Synthesis of $HPCrCo_2(CO)_{11}$. In a typical preparation, 0.837 g (3.70 mmol) of $H_3PCr(CO)_5$ and 0.901 g (2.64 mmol) of $Co_2(CO)_8$ were placed in a 50-mL round-bottom flask fitted with several break-off seals and a magnetic stirring bar. These operations were effected in a dry nitrogen atmosphere box. This reaction flask then was attached to the vacuum apparatus and evacuated. The flask was cooled to −79 °C and freshly distilled dry tetrahydrofuran was condensed onto the reactants. When the reaction flask was allowed to warm to room temperature, an immediate reaction ensued as evidenced by a slow but steady evolution of a noncondensable gas. Periodically, during the next 60 h, the reaction vessel was cooled to −196 °C and the noncondensable product gas removed. After each removal the vessel was allowed to warm to and remain at room temperature with vigorous stirring. When no further noncondensable gas was formed the stirring was discontinued. During the 60-h reaction period the solution in the vessel darkened from red to dark blood red. The total gas collected during the 60 h of reaction consisted of a mixture of 2.66 mmol of hydrogen gas and 5.26 mmol of carbon monoxide.

Removal of the tetrahydrofuran from the reaction vessel left a dark blood red crystalline solid. The reaction vessel then was heated to 50 °C and material volatile at the temperature removed. This material was separated by fractional condensation techniques into 0.242 g (1.07 mmol) of $H_3PCr(CO)_5$ and a small amount of tetrahydrofuran. Any unreacted $Co_2(CO)_8$ should also have been removed in this step.

Thus, 2.64 mmol of $Co_2(CO)_8$ and 2.63 mmol of $H_3PCr(CO)_5$ (3.70–1.07) were consumed in the reaction. From these data and the amount of hydrogen and carbon monoxide produced, the empirical composition of the crystalline product is $H_{0.97}P_{1.00}Cr_{2.00}(CO)_{11.03}$.

The product is evidently homogeneous since all of the residue could be dissolved in either methylene chloride or hexane.

Analysis of the dark red solid for carbon monoxide content, using the method of Hallock[6] involving oxidation by iodine in pyridine solution, gave a carbon monoxide count of 10.84 compared with 11.00 for $HPCrCo_2(CO)_{11}$.

Total elemental analysis by an outside laboratory gave results in good agreement with the empirical formula. Anal. Calcd: H, 0.20; P, 6.08; Cr, 10.2; Co, 23.2; C, 25.9; O, 34.5. Found: H, 0.30; P, 5.30; Cr, 8.0; Co, 25.2; C, 26.5; O, 34.7.

The mass spectrum, obtained using a direct solids inlet and an ionizing potential of 70 eV, is shown in Table I. The molecular ion at a mass number of 510 established $HPCrCo_2(CO)_{11}$ as the molecular formula.

A methylene chloride solution gave infared absorptions at 2110 (w), 2069 (sh), 2030 (sh), 1974 (m), and 1952 (s) cm^{-1}.

The proton NMR spectrum of a CCl_3D solution consisted of a doublet centered at τ 5.85 with a $J(P{-}H)$ = 276 Hz.

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Registry No. I, 63989-16-2; $H_3PCr(CO)_5$, 18116-53-5; $Co_2(CO)_8$, 10210-68-1.

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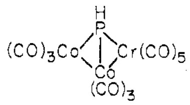
(3) One of the reviewers of this paper has taken exception to our suggested structure. He prefers the following structure possessing five-coordinate and six-coordinate cobalt atoms with a seven-coordinate chromium atom.



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Contribution from the Department of Chemistry,
University of Southern California,
Los Angeles, California 90007

Photochemistry of Complex Ions. 16. $Cr(NH_3)_5F^{2+}$

Robin E. Wright and Arthur W. Adamson*

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The ligand field photochemistry of chromium(III) ammines has been extensively studied,[1] particularly with respect to supporting, disproving, modifying, or explaining Adamson's photolysis rules.[1] Early exceptions to these rules were *trans*-$Cr(cyclam)Cl_2^+$ [2] (being nearly photoinert) and *trans*-$Cr(en)_2F_2^+$.[3] The photoproduct in this last case is *trans*-$Cr(en)(enH)(H_2O)F_2^{2+}$ rather than *cis*-$Cr(en)_2(H_2O)F^{2+}$, as expected in analogy to the behavior of *trans*-$Cr(en)_2Cl_2^+$.[4] However, the lowest quartet excited state for *trans*-$Cr(en)_2F_2^+$ is σ antibonding in $d_{x^2-y^2}$ rather than in d_{z^2},[5] the more usual for chromium(III) ammines. This assignment has provided a basis for explaining the anomalous photochemistry.[3,6,7]

It seemed surprising that the photochemistry of $Cr(NH_3)_5F^{2+}$ had not been studied in view of the special behavior of fluoride as a ligand and the extensive investigations of other members of the $Cr(NH_3)_5X^{2+}$ series.[1] The present investigation was undertaken to remedy this omission. An additional point of interest was whether the photochemistry of $Cr(NH_3)_5F^{2+}$ might show some informative pH behavior. Since fluoride is both an atomic ligand and the anion of a weak acid, there was the possibility of acid-catalyzed photochemistry. The thermal substitution chemistry is predominantly one of fluoride aquation ($k = 2.46 \times 10^{-7}\ s^{-1}$ at 25 °C [8]) and is indeed acid catalyzed.

Experimental Section

Preparations. Aquopentaamminechromium(III) Nitrate. The preparation was by the method of Mori[9] and provided the starting material for the next preparation.

Fluoropentaamminechromium(III) Perchlorate. This complex was prepared from the aquopentaammine by a literature procedure.[10] The salt was recrystallized twice from a saturated solution by the dropwise addition of a filtered saturated sodium perchlorate solution. The product was then recrystallized by cooling a saturated solution to 5 °C. The needle-shaped crystals were washed with ethanol and ether, then air-dried. The final yield was 18%. The product contained less than 0.1% of free fluoride and the absorption spectrum in 0.01 M perchloric acid was in excellent agreement with the literature[10] (band maximum in nm (extinction coefficient, $M^{-1}\ cm^{-1}$)): 502 (41.7), 367 (21.0). Anal. Calcd for $[Cr(NH_3)_5F](ClO_4)_2$: Cr, 14.65; F, 5.35. Found: Cr, 14.95; F, 5.18.

Analytical Methods. Free ammonia was determined by the indophenol spectrophotometric method,[11] which was calibrated against a known ammonium chloride solution. In order to correct for pH effects, calibration curves were prepared for each pH used.

Photoreleased fluoride was measured with an Orion Model 96-09 combination fluoride electrode connected to a Beckman Model 1019 research pH meter. In order to obtain stable millivolt readings, it

Table I. Photochemistry of $Cr(NH_3)_5X^{2+}$ Complexes (Irradiation of First Ligand Field Band)

X	ϕ_{NH_3}	ϕ_{NH_3}/ϕ_X	Confign of principal photoproduct	Ref
F	0.44[a]	105[a]	Cis	This work
Cl	0.36	1000,[b] 70[c]	Cis	1
Br	0.35	39	Cis	1
NCS	0.48	23	Cis	1

[a] In 0.010 M $HClO_4$. [b] C. F. C. Wong and A. D. Kirk, *Can. J. Chem.*, 52, 3384 (1974). An earlier value of 70 may be low because of thermal chloride release from the photoproducts. [c] H. F. Wasgestian and H. L. Schläfer, *Z. Phys. Chem. (Frankfurt am Main)*, 62, 127 (1968).

was necessary to remove unreacted complex from the solutions prior to analysis. This was accomplished by passing both the dark and photolyzed solutions through short (5 mm in height, 1 cm in diameter) columns of dry Dowex 50W-X2 cation-exchange resin in the Na^+ form. Better than 99% of the free fluoride present was collected by applying air pressure to the column head and allowing complete elution from the resin. Aliquots of the eluate were then buffered to pH 5–5.5, and the ionic strength was adjusted to 0.5 M with a solution prepared according to the electrode manual. Since the electrode response was nonlinear in the concentration region of interest, frequent calibrations were done, again, at each pH used for photolysis.

Total fluoride content was determined by the zirconium–eriochrome cyanine R photometric technique.[12] The complex was destroyed by gently heating on a sand bath an aliquot with an equivalent volume of 1 N NaOH to dryness in a platinum crucible. The residue was taken up in water and treated in the manner described.

Chromium was determined by a published procedure.[13] Oxidation with ammonium persulfate in the presence of silver nitrate oxidized the Cr(III) to Cr(VI), which was then determined spectrophotometrically with 1,5-diphenylcarbohydrazide. In order to obtain reproducible results, it was necessary to use freshly recrystallized (from ethanol) 1,5-diphenylcarbohydrazide as the extinction coefficient of the Cr(VI) complex at the absorption maximum was found to decrease fairly rapidly with the age of the complexing agent.[14] Ordinarily, persulfate oxidation will destroy a chromium(III) ammine, but in the case of $Cr(NH_3)_5F^{2+}$, it was necessary to decompose the complex in molten sodium hydroxide in a platinum crucible. The residue was taken up in 0.5 N sulfuric acid and analyzed by the persulfate oxidation procedure.

Photolysis Procedures. Irradiations were at 514.5 nm by means of an Ar ion laser (Coherent Radiation Model 52-G); the beam was expanded by a lens so as to nearly cover the window of the spectrophotometer cell. Incident light intensities were read from an internal power meter which had been calibrated by Reineckate actinometry.[13] Photolyses were restricted to under 15% total reaction to minimize changes in light absorption, inner-filter effects, and possible secondary photolysis. This last was not important since isosbestic points were maintained beyond 20% photolysis. Absorption spectra were obtained by means of a Beckman Acta MVI instrument.

Solutions irradiated were 0.001–0.003 M in $Cr(NH_3)_5F^{2+}$, while 0.10 M perchloric acid, 0.010 M perchloric acid, and water were used as solvents. If ammonia release was to be determined, a 5-cm cell of 13.7-cm^3 volume was used for irradiation, allowing duplicate analyses on 5-cm^3 aliquots. For fluoride release, a larger volume of sample was required. Therefore, a 10-cm cell of 27.2-cm^3 volume was used. In both cases, the irradiation cell was positioned in a thermostated holder kept at 24.2 ± 0.5 °C. Irradiation times were typically 250 s.

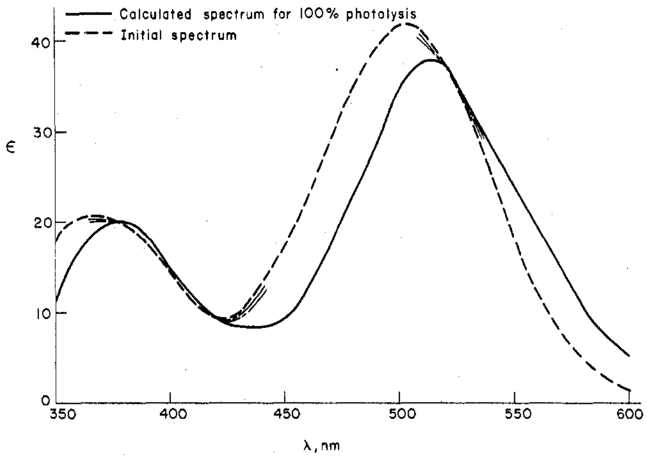

Figure 1. Initial spectrum of $[Cr(NH_3)_5F](ClO_4)_2$ in 0.010 M $HClO_4$ and calculated spectrum for 100% photolysis. The short segments illustrate that the isosbestic points were maintained during photolysis.

Results and Discussion

The results are summarized in Table I. At pH 2, the yield for ammonia photoaquation is 0.44[15] and of fluoride, 0.0042. In the series $Cr(NH_3)_5X^{2+}$, for X = Cl, Br, and NCS the principal photoproduct is *cis*-$Cr(NH_3)_4(H_2O)X^{2+}$. The same appears to be true for X = F based on spectral evidence. Figure 1 shows the initial spectrum and that calculated for pure photoproduct by extrapolating the spectral changes for 10–15% photolysis. Table II summarizes relevant spectral data and it seems clear that the photoproduct is primarily *cis*-$Cr(NH_3)_4(H_2O)F^{2+}$. First, were it the trans isomer, the first ligand field absorption band (L_1 band) should have moved to a much longer wavelength than it did and dropped to half the intensity, both contrary to observation. Furthermore, the ratios of extinction coefficients for the L_1 and L_2 band maxima are 1.97 and 0.77 for the *cis*- and *trans*-fluoroaquo complexes, respectively. The calculated spectrum for 100% photolysis gives a peak ratio of 1.92. It seems safe to estimate that no more than 20% of the photoproduct could have been in the trans form.

Thus, the photochemistry of $Cr(NH_3)_5F^{2+}$ is quite analogous to other members of the $Cr(NH_3)_5X^{2+}$ series and, in particular, to the $Cr(NH_3)_5Cl^{2+}$. In this last case, it was established that it is the trans ammonia that photoaquates.[16] It seems a reasonable, although not proven, conclusion that the same is true for the fluoropentaammine complex. Polarized spectra studies on the fluoropentaammine were used to assign the first excited quartet state to be σ antibonding in d_{z^2}, in analogy to $Cr(NH_3)_5Cl^{2+}$. However, the data has been reinterpreted more recently to indicate that the ordering is similar to that of *trans*-$Cr(en)_2F_2^+$; i.e., the first excited quartet state is σ antibonding in $d_{x^2-y^2}$.[17] Regardless of the ordering predicted from polarized spectra, it is important to recognize that the lowest quartet in the absorption spectrum is not necessarily the lowest for the thermally equilibrated quartet from which reaction occurs.

Table II. Spectral Characteristics

Complex	Wavelength, nm (ε, M^{-1} cm^{-1}) Max	Min	Max	Ref
$Cr(NH_3)_5F^{2+}$	367 (21.0)	420 (9.0)	502 (41.7)	This work
Photoproduct (calcd)	374 (20.0)	434 (8.5)	514 (38.4)	
trans-$Cr(NH_3)_4(H_2O)F^{2+}$	377 (27.9)		529 (21.6), 485 sh (20.2)	*a*
cis-$Cr(NH_3)_4(H_2O)F^{2+}$	375 (21.0)	431 (10.7)	512 (41.3)	*b*

[a] G. Wirth, C. Bifano, R. T. Walters, and R. G. Linck, *Inorg. Chem.*, **12**, 1955 (1973). [b] H. N. Poyung-Hsien Chung and S. R. Davis, *J. Inorg. Nucl. Chem.*, 35, 2849 (1973).

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.

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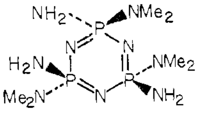
A large number of aminophosphazenes have been synthesized by the interaction of halocyclophosphazenes with primary or secondary amines.[2] The thermal behavior of this class of compounds is of some interest since specific aminocyclophosphazenes are useful as flame retardants and others have a biomedical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

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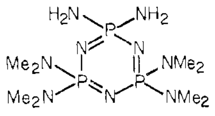
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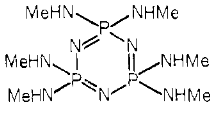
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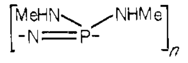
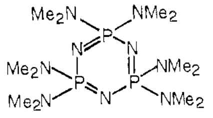
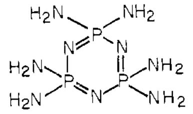

IV

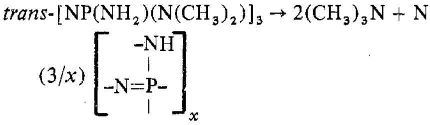
($n \approx$ 10 000)


V

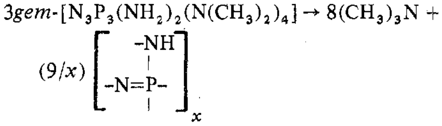

VI

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]

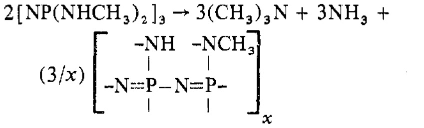
Table I lists the amounts of volatile pyrolysis products obtained at 310 °C from the aminophosphazenes studied, together with comparative published data for $[NP(NH_2)_2]_3$ (VI). These results are incorporated into eq 1–6.



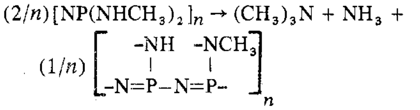
$$trans\text{-}[NP(NH_2)(N(CH_3)_2)]_3 \rightarrow 2(CH_3)_3N + NH_3 + (3/x)\left[\begin{matrix}\text{-NH}\\ |\\ \text{-N=P-}\\ |\end{matrix}\right]_x \qquad (1)$$



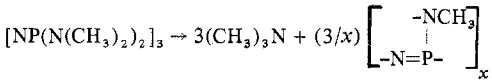
$$3gem\text{-}[N_3P_3(NH_2)_2(N(CH_3)_2)_4] \rightarrow 8(CH_3)_3N + NH_3 + (9/x)\left[\begin{matrix}\text{-NH}\\ |\\ \text{-N=P-}\\ |\end{matrix}\right]_x \qquad (2)$$



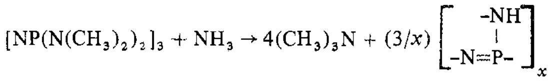
$$2[NP(NHCH_3)_2]_3 \rightarrow 3(CH_3)_3N + 3NH_3 + (3/x)\left[\begin{matrix}\text{-NH} & \text{-NCH}_3\\ | & |\\ \text{-N=P-} & \text{N=P-}\\ | & |\end{matrix}\right]_x \qquad (3)$$



$$(2/n)[NP(NHCH_3)_2]_n \rightarrow (CH_3)_3N + NH_3 + (1/n)\left[\begin{matrix}\text{-NH} & \text{-NCH}_3\\ | & |\\ \text{-N=P-} & \text{N=P-}\end{matrix}\right]_n \qquad (4)$$

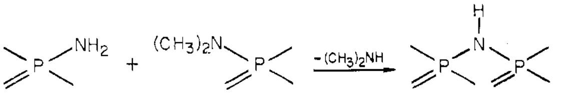


$$[NP(N(CH_3)_2)_2]_3 \rightarrow 3(CH_3)_3N + (3/x)\left[\begin{matrix}\text{-NCH}_3\\ |\\ \text{-N=P-}\end{matrix}\right]_x \qquad (5)$$



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

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 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



(7)