tonitrile.[25] In acetonitrile, solvolysis is minimized and the product can be isolated.

Acknowledgment. We wish to thank the National Science Foundation for support of this research.

Pulsed-Laser Conductivity and Emission Study of Some Chromium(III) Amine Complex Ions in Acidic and Alkaline Aqueous Media

WILLIAM L. WALTZ,*[1a] JOCHEN LILIE,[1b] and SANG H. LEE[1a]

Received August 10, 1983

The photochemistry and photophysics of Cr(tn)$_3$$^{3+}$, *trans*-Cr(en)$_2F_2$$^+$, Cr(en)$_3$$^{3+}$, Cr(NH$_3$)$_6$$^{3+}$, Cr(NH$_3$)$_5(CN)^{2+}$, and Cr(NH$_3$)$_5(NCS)^{2+}$, where en and tn designate ethylenediamine and 1,3-propanediamine ligands, respectively, have been studied in acidic aqueous media with use of conductivity and emission detection methods in conjunction with pulsed-laser excitation at 347 nm and at 530 nm. The last five complex ions have also been investigated in alkaline solutions. For acidic conditions, the conductivity decreases in two distinct stages with the exception of only one stage for *trans*-Cr(en)$_2$F$_2$$^+$. The longer term stage has the same lifetime as that for emission decay, and it represents the major component to photochemical reaction (67–100%). In this regard, the issue of direct chemical reaction from doublet electronically excited states vs. one of thermal back intersystem crossing from the doublet to low-lying quartet levels, followed by ligand substitution, is discussed. The initial short-term decreases in conductivity are attributed to protonation of released ammonia and of the monodentate en and tn ligands (k_{H^+} = (0.3–2) × 10^{10} M^{-1} s^{-1}) subsequent to their prompt formation from short-lived quartet states. In basic media, both the emission intensities and the lifetimes decrease with increasing hydroxide ion concentration, except for *trans*-Cr(en)$_2$F$_2$$^+$. The rate constants for emission quenching range from about 0.2 × 10^{10} to 2 × 10^{10} M^{-1} s^{-1}. The conductivity results indicate that, with the possible exception of Cr(NH$_3$)$_5$(NCS)$^{2+}$, hydroxide ion quenching of emission and chemical reaction does not induce net chemical change.

Introduction

The photochemistry and photophysics of chromium(III) amine type complex ions in aqueous and nonaqueous media have been for many years the focus of a large number of both experimental and theoretical studies.[2-9] In part, this intense activity is made feasible by the availability of six-coordinate chromium(III) complex ions, having a wide variety of different ligand systems. In contrast to the relatively inert thermal behavior of the complexes toward substitution reactions, irradiation in the UV–visible region of the quartet and doublet ligand field bands gives rise to substantial levels of photochemical reaction, generally that of photosolvolysis or photoanation, and this is frequently accompanied by emission, usually from the lower energy and spin-forbidden doublet states. The situation is exemplified by the numerous studies of Cr(NH$_3$)$_6$$^{3+}$, Cr(NH$_3$)$_5(CN)^{2+}$, Cr(NH$_3$)$_5(NCS)^{2+}$, *trans*-Cr(en)$_2F_2$$^+$, Cr(en)$_3$$^{3+}$, and Cr(tn)$_3$$^{3+}$, where en and tn are ethylenediamine and 1,3-propanediamine, respectively, which are the subject of this report.[2,5,6,9,10-38]

While the photochemical and photophysical investigations on these and related systems have contributed very significantly

(1) (a) University of Saskatchewan. (b) Hahn-Meitner-Institut.
(2) Adamson, A. W. *Comments Inorg. Chem.* **1981**, *1*, 33.
(3) Hollebone, B. R.; Langford, C. H.; Serpone, N. *Coord. Chem. Rev.* **1981**, *39*, 181.
(4) Jamieson, M. A.; Serpone, N.; Hoffman, M. Z. *Coord. Chem. Rev.* **1981**, *39*, 121.
(5) Kirk, A. D. *Coord. Chem. Rev.* **1981**, *39*, 225.
(6) Kemp, T. J. *Prog. React. Kinet.* **1980**, *10*, 301.
(7) Vanquickenborne, L. G.; Ceulemans, A. *J. Am. Chem. Soc.* **1977**, *99*, 2208.
(8) Vanquickenborne, L. G.; Ceulemans, A. *Coord. Chem. Rev.* **1983**, *48*, 157.
(9) Zinato, E. In "Concepts of Inorganic Photochemistry"; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley: New York, 1975; Chapter 4.
(10) Linck, N. J.; Berens, S. J.; Magde, D.; Linck, R. G. *J. Phys. Chem.* **1983**, *87*, 1733.

(11) Angermann, K.; Schmidt, R.; van Eldik, R.; Kelm, H.; Wasgestian, F. *Inorg. Chem.* **1982**, *21*, 1175.
(12) Forster, L. S.; Rund, J. V.; Castelli, F.; Adams, P. *J. Phys. Chem.* **1982**, *86*, 2395.
(13) Kirk, A. D.; Rampi Scandola, M. A. *J. Phys. Chem.* **1982**, *86*, 4141.
(14) Kirk, A. D. *J. Phys. Chem.* **1982**, *86*, 3638.
(15) Yang, X.; Sutton, C. A.; Kutal, C. *Inorg. Chem.* **1982**, *21*, 2893.
(16) Adamson, A. W.; Fukuda, R. C.; Walters, R. T. *J. Phys. Chem.* **1981**, *85*, 3206.
(17) Angermann, K.; van Eldik, R.; Kelm, H.; Wasgestian, F. *Inorg. Chem.* **1981**, *20*, 955.
(18) Cimolino, M. C.; Linck, R. G. *Inorg. Chem.* **1981**, *20*, 3499.
(19) Kirk, A. D. *J. Phys. Chem.* **1981**, *85*, 3205.
(20) Krause, H. H.; Wasgestian, F. *Inorg. Chim. Acta* **1981**, *49*, 231.
(21) Kühn, K.; Wasgestian, F.; Kupka, H. *J. Phys. Chem.* **1981**, *85*, 665.
(22) Kirk, A. D.; Porter, G. B. *J. Phys. Chem.* **1980**, *84*, 887.
(23) Pyke, S. C.; Linck, R. G. *Inorg. Chem.* **1980**, *19*, 2468.
(24) Riccieri, P.; Zinato, E. *Inorg. Chem.* **1980**, *19*, 3279.
(25) Zinato, E.; Adamson, A. W.; Reed, J. L.; Puaux, J. P., submitted for publication.
(26) Waltz, W. L.; Walters, R. T.; Woods, R. J.; Lilie, J. *Inorg. Chim. Acta* **1980**, *46*, L153 and references therein.
(27) Fukuda, R.; Walters, R. T.; Mäcke, H.; Adamson, A. W. *J. Phys. Chem.* **1979**, *83*, 2097.
(28) Kirk, A. D.; Frederick, L. A.; Wong, C. F. C. *Inorg. Chem.* **1979**, *18*, 448.
(29) Walters, R. T.; Adamson, A. W. *Acta Chem. Scand., Ser. A* **1979**, *A33*, 53.
(30) Sandrini, D.; Gandolfi, M. T.; Balzani, V. *J. Am. Chem. Soc.* **1977**, *99*, 4523.
(31) Kane-Maguire, N. A. P.; Richardson, D. E.; Toney, C. G. *J. Am. Chem. Soc.* **1976**, *98*, 3996.
(32) Kane-Maguire, N. A. P.; Phifer, J. E.; Toney, C. G. *Inorg. Chem.* **1976**, *15*, 593.
(33) Ballardini, R.; Varani, G.; Wasgestian, H. F.; Moggi, L.; Balzani, V. *J. Phys. Chem.* **1973**, *77*, 2947.
(34) Zinato, E.; Riccieri, P. *Inorg. Chem.* **1973**, *12*, 1451.
(35) Langford, C. H.; Tipping, L. *Can. J. Chem.* **1972**, *50*, 887.

to the understanding of the behavior of electronically excited chromium(III) complex ions, controversy continues to exist concerning the relative importance of the doublet and quartet states to the photochemical events and the related issue of the role of thermally activated back intersystem crossing from the vibrationally equilibrated doublet states (thexi) to those of the quartet levels. In this work, we have addressed these issues in a time-resolved manner through the use of pulsed-laser excitation at 347 and/or 530 nm in conjunction with conductivity and emission detection methods. The results both complement and extend those of earlier studies such as ones based on quenching of emission and chemical reaction and in the case of $Cr(en)_3^{3+}$ the time-resolved investigation of the product formation observed by optical absorption[27] as well as in our preliminary report on the photoconductivity of this complex ion in acidic media.[26] In this regard, a more complete description of the conductivity methods used in this work and in several previous studies on other systems is provided.[39,40]

For the chromium(III) amine complexes studied here, the major or sole photochemical process is photoaquation, resulting either in the release of ammonia or in the formation of monodentate en or tn ligand species. In acidic media, the conductivity detection methods monitor primarily the subsequent protonation processes for these photoproducts. While the rates of the protonation reactions are in general very high, it has been possible by variation of the initial pH of the solutions to investigate to some extent the dynamics of protonation as well as those of the photoevents.

For certain of the complex ions, the studies have been extended to alkaline media containing sodium hydroxide, and in this circumstance, alterations in conductivity will reflect principally temporal changes in hydroxide ion concentration. The motivation for studying this aspect derives from the fact that hydroxide ion has previously been employed as a quenching agent for both emission and chemical reaction; however, concerns have been expressed as to whether or not the action of hydroxide ion is chemically of an innocent or noninnocent behavior.[5,20,25,27,30,32,35] It has been proposed that hydroxide ion quenching of the doublet state for $Cr(NH_3)_6^{3+}$ can involve the formation of an amido species, $Cr(NH_3)_5$-$(NH_2)^{2+}$, and a similar proposal has been put forward with respect to $Rh(NH_3)_5(Cl)^{2+}$.[35,41] Our conductivity and emission findings indicate that, with the possible exception of $Cr(NH_3)_5(NCS)^{2+}$, quenching at the doublet state level does not induce further net chemical change; i.e., it is operationally of an innocent type of mechanism.

Experimental Section

Materials and Solutions. Hexaamminechromium(III) perchlorate, $[Cr(NH_3)_6](ClO_4)_3$, was prepared by the method of Oppegard and Bailar, and the purity of the material was found to be satisfactory as determined by its UV–visible absorption spectrum and by analysis of its chromium content.[42] The sample of tris(ethylenediamine)-chromium(III) perchlorate, $[Cr(en)_3](ClO_4)_3$, was that used in our earlier report.[26] Limited amounts of the following compounds were used as received: *trans*-difluorobis(ethylenediamine)chromium(III) perchlorate, $[Cr(en)_2F_2]ClO_4$, from Dr. A. D. Kirk; tris(1,3-propanediamine)chromium(III) perchlorate, $[Cr(tn)_3](ClO_4)_3$, from Dr. F. Wasgestian; cyanopentaamminechromium(III) perchlorate, $[Cr(NH_3)_5(CN)](ClO_4)_2$, from Dr. E. Zinato. Two different sources of (isothiocyanato)pentaamminechromium(III) perchlorate, $[Cr(N-H_3)_5(NCS)](ClO_4)_2$, were employed. One sample was provided by
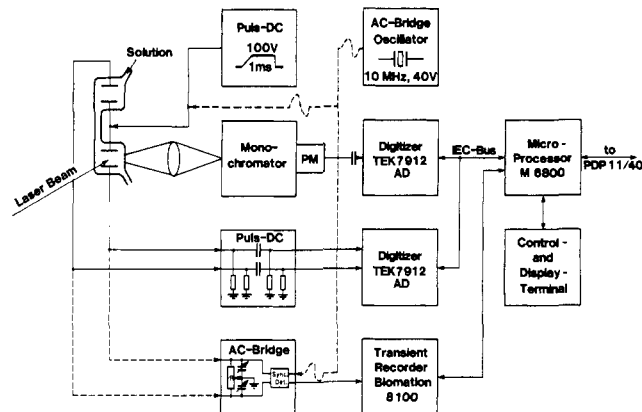

Figure 1. Schematic representation of experimental apparatus and of the system for data analysis and collection.

Dr. A. W. Adamson. The absorption spectrum of this sample agreed with that reported;[37] however, the elemental analyses for Cr, N, and C were about 1–2% higher than those expected. A second sample, prepared as described by Zinato, Lindholm, and Adamson,[37] gave good results for elemental Cr, N, and C content but the molar absorption coefficients of the peaks (484 and 364 nm) were about 10% low relative to those of the other sample. While these differences suggest the possibility of some impurity in either or both samples, the feature of importance to this study is that the two samples gave in general the same results in terms of their kinetic behavior.

Solutions of the complex ions were prepared just prior to use with water purified by a Millipore Super-Q system, and their pHs were adjusted by the addition of reagent grade NaOH or $HClO_4$. In one experiment involving $Cr(NH_3)_5(NCS)^{2+}$, H_2SO_4 was employed in place of $HClO_4$. Because the signal sensitivity of the conductivity apparatus at electrolyte concentrations above 2×10^{-3} M depends on the total conductance of the solutions, care was taken to ensure that signal comparisons between acidic and basic media were made on solutions of comparable conductance levels. The decrease in detection sensitivity at high conductance levels restricted the pH range to values between about 2.3 and 11.7, with the pH region from 4.5 to 9.5 being avoided in order to minimize possible kinetic complications associated with the autoionization reaction of water. The irradiation studies were performed under deaerated conditions (argon atmosphere) over the temperature range 20–24 °C with the samples being exposed to as little extraneous light as possible.

Photolysis Apparatus. In Figure 1, a schematic representation is presented of the components used to carry out the conductivity and optical experiments, coupled with on-line computer-based data acquisition and analysis. The laser sources, used at the Hahn-Meitner Institut, were a frequency-doubled Q-switched neodymium-yag unit with an output of ca. 100 mJ/flash (duration ca. 20 ns) at 530 nm and a frequency-doubled ruby system delivering at 347 nm a pulse of ca. 70 mJ/flash (duration ca. 15 ns).[26] The laser intensity was measured by a photodiode. In general, the intensity of the laser was varied by a factor of 2–7, and with the exception of one case (see below), nonlinear effects were not observed. The irradiation vessel, employed for both optical and conductivity experiments, was a flow-through quartz cell consisting of two very similar compartments. Both compartments contained a pair of platinum electrodes (approximately 6 mm × 6 mm surface area with about 6-mm separation between the electrode surfaces). The laser beam irradiated a spot of about 6 mm diameter between the electrodes of the lower compartment. The upper, unirradiated compartment served as an ac conductivity reference. The optical and dc conductivity detection systems are described elsewhere.[26] The latter employed a 100-V pulse of about 5 ms duration, during which time the solution was irradiated, and the observation period lasted for about 20 μs. The ac conductivity method provided the means whereby changes could be measured over much longer time periods (ca. 1 μs to 1 s) after the laser pulse. The apparatus and concept for this technique were similar to those described previously for use in pulse radiolysis.[43] In the ac method, the electrodes from the two-cell compartments formed the arms of a bridge that can be balanced by resistor R and two associated capacitors. A

(36) Martin, J. E.; Adamson, A. W. *Theor. Chim. Acta* **1971**, *20*, 119.
(37) Zinato, E.; Lindholm, R. D.; Adamson, A. W. *J. Am. Chem. Soc.* **1969**, *91*, 1076.
(38) Gowin, E.; Wasgestian, F., personal communication.
(39) Lilie, J. *J. Am. Chem. Soc.* **1979**, *101*, 4419.
(40) Lilie, J.; Waltz, W. L. *Inorg. Chem.* **1983**, *22*, 1473.
(41) Adamson, A. W.; Fukuda, R. C.; Larson, M.; Mäcke, H.; Puaux, J. P. *Inorg. Chim. Acta* **1980**, *44*, L13.
(42) Oppegard, A. L.; Bailar, J. C., Jr. *Inorg. Synth.* **1950**, *3*, 153.

(43) Lilie, J.; Fessenden, F. W. *J. Phys. Chem.* **1973**, *77*, 674.

Table I. Some Selected Photochemical, Photophysical, and Spectroscopic Information

complex ion (microsymmetry)	doublet level em peak, nm	τ, μs	quartet levels abs peak, nm	$\Phi_{chem}{}^a$ (quartet region)	photoproduct(s) in acidic media
$Cr(NH_3)_6{}^{3+}$ (O_h)	667^b	2.2^c	464, 352	NH_3, 0.45^d	$Cr(NH_3)_5(H_2O)^{3+}$ [e]
$Cr(NH_3)_5(CN)^{2+}$ (C_{4v})	680^f	18^g	451, 347^f	NH_3, 0.37^g	$Cr(NH_3)_4(H_2O)(CN)^{2+}$ [g] (28% trans, 72% cis)
$Cr(NH_3)_5(NCS)^{2+}$ (C_{4v})	688^b	0.26^c	485 364	NH_3, $0.42/NCS^-$, 0.02^h NH_3, $0.46/NCS^-$, 0.030^i	$cis\text{-}Cr(NH_3)(H_2O)(NCS)^{2+}/Cr(NH_3)_5(H_2O)^{3+}$ [i,j]
$Cr(en)_3{}^{3+}$ (O_h)	670^b	1.85^c	456, 350	en, 0.37^k	$Cr(en)_2(enH)(H_2O)^{4+}$ (27% Λ-cis, 8% Δ-cis, 65% trans)^k
$trans\text{-}Cr(en)_2F_2{}^+$ (D_{4h})	788^b	1.28^e	525, 466^l	en, 0.35^m	$Cr(en)(enH)(H_2O)F_2{}^{2+}$ [m]
$Cr(tn)_3{}^{3+}$ (O_h)	666^n		462, 353	tn, ca. 0.15^o	$Cr(tn)_2(tnH)(H_2O)^{4+}$ [o]

^{a} Unless otherwise inidcated, Φ_{chem} is nearly independent of excitation wavelength. ^{b} Reference 22. ^{c} Reference 29. ^{d} Reference 20. ^{e} Reference 10. ^{f} Reference 24. ^{g} Calculated for 23 °C.^{25} ^{h} λ(irrad) = 546 nm.^{17} ^{i} λ(irrad) = 373 nm.^{37} ^{j} Reference 34. ^{k} Reference 18. ^{l} The L_1 band is composed of two components with the lower energy transition being $^4E_g(^4T_{2g}) \leftarrow {}^4B_{1g}$ and the higher one being $^4B_{2g}(^4T_{2g}) \leftarrow {}^4B_{1g}$.^{44} ^{m} The photoproduct cited is the major product (>80%) for photolysis at 520 nm although it occurs in several isomeric forms with the trans configuration being the dominant one.^{23} ^{n} Reference 21. ^{o} Reference 38.

10-MHz sine-wave generator delivered a 40-V (peak–peak) signal to the middle electrodes with high frequency stability (quartz controlled) and low distortion (<–60 dB) (Figure 1). The signal difference from the outer electrodes was amplified and rectified by a synchronous detector. For this purpose, a reference signal that could be shifted in phase relative to the measuring wave form was applied to the detector circuit. The amplified output of this detector was digitized in a Biomation 8100 transient recorder. This information (and similar output from the optical detection system) was transferred via a microprocessor to a PDP 11/40 computer. The latter controlled signal averaging and allowed for on-line data evaluation. The figures, given in Results showing the kinetic changes in conductivity, exemplify in an abridged manner the resulting display of the data and its analysis: The open circles represent data points and the solid lines are calculated fits for first-order rate laws with the end levels being specified by a horizontal line. Estimates to the standard deviations, cited for the data, are based on pooling of the results from different experimental periods, with the number of such periods being given within parentheses. For a particular period and experiment, a number of individual measurements (typically 3–5) were made, and the precision of the data at this level was approximately the same as that from the combined sets of data.

Results

Background information pertinent to the results and discussion of this study is present in Table I. A notable feature is that radiation of 347 nm corresponds generally to irradiation of the L_2 band (quartet) near the peak maximum whereas that of 530 nm falls to the red side of the L_1 peak (quartet). The wavelength of 530 nm is also well removed from the weak doublet bands. The corresponding emission bands listed in Table I give the approximate location of the absorption bands with the exception of $trans\text{-}Cr(en)_2F_2{}^+$. While the luminescence yields are quite small and thus emission is a minor process,^{22,25} its occurrence served in this study as a useful marker to correlate the excited-state behavior with the conductivity changes.

Within the context of O_h microsymmetry, the L_1 and L_2 bands involve the transitions $^4T_{2g} \leftarrow {}^4A_{2g}$ and $^4T_{1g} \leftarrow {}^4A_{2g}$, respectively. Under lower symmetry, the degeneracies of the ^4T levels are lifted. For $Cr(NH_3)_5(CN)^{2+}$ and $Cr(NH_3)_5(NCS)^{2+}$, the resulting splitting of the bands is not observed for room-temperature solutions; however, on theoretical grounds, the ordering of the component energy levels is expected to be reversed between these two complexes.^{7,44} With $trans\text{-}Cr(en)_2F_2{}^+$, the splitting of the L_1 band (and L_2) is readily discernible (Table I).

For the complexes of interest here, the results of steady-state photolysis experiments indicate that the photochemistry involves substitution by H_2O (or OH^-) at a nitrogen coordination site, resulting in a release of ammonia or in the formation of
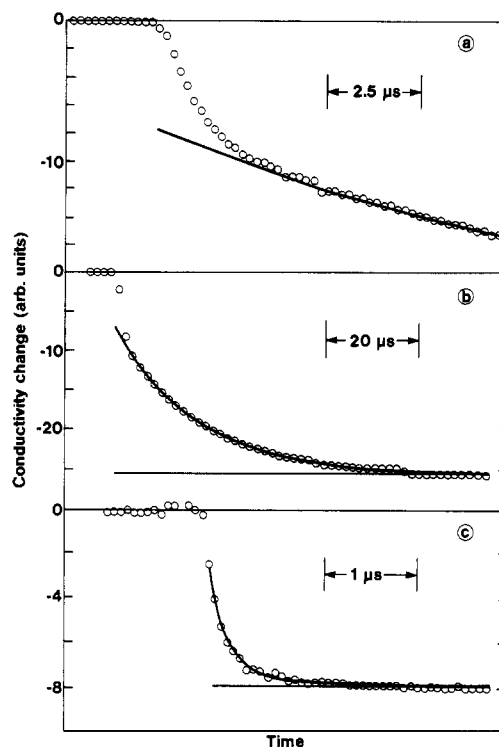

Figure 2. Decreases in conductivity following pulsed-laser excitation at 347 nm of 2.5 mM $Cr(NH_3)_5(CN)^{2+}$: (a, b) short- and long-term changes at pH 3.1; (c) change at pH 10.2 (the scale of the vertical axis is not directly comparable to those of (a) and (b)).

an amine ligand attached at only one position. While photolytic loss of NCS^- from $Cr(NH_3)_5(NCS)^{2+}$ occurs, it is very minor relative to release of ammonia (Table I). Such substitution for cyanide in the congeneric $Cr(NH_3)_5(CN)^{2+}$ case is not found nor is the loss of fluoride a prominent factor with $trans\text{-}Cr(en)_2F_2{}^+$.^{23,24} Under our acid conditions, protonation of released ammonia or of the uncoordinated nitrogen of the monodentate en and tn ligands will readily transpire^{26,45} and lead to a decrease in conductivity. In basic media (pH ≥9.5), such protonation will not be substantial; however, deprotonation of coordinated water in the photoproducts can now occur to initiate a decrease in conductivity through consumption of hydroxide ion.$^{46-53}$ For these reasons, we will consider the

(44) Perumareddi, J. R. *Coord. Chem. Rev.* **1969**, *4*, 73.

(45) Eigen, M. *Angew. Chem.* **1963**, *75*, 489.
(46) pK_a of $Cr(NH_3)_5(H_2O)^{3+}$ = 5.3.^{47}
(47) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967; p 32.
(48) pK_a for $trans\text{-}Cr(NH_3)_4(H_2O)(CN)^{2+}$ = 5.5; pK_a for $cis\text{-}Cr(NH_3)_4(H_2O)(CN)^{2+}$ = 5.6.^{49}
(49) Zinato, E., personal communication.

Table II. Lifetimes for Conductivity and for Emission in Acidic Media[a]

complex ion	347-nm excitation		530-nm excitation	
	τ(cond), μs	τ(em), μs	τ(cond), μs	τ(em), μs
$Cr(NH_3)_6^{3+}$	2.1 ± 0.3 (4)[b]	2.0 ± 0.1 (3)[b]	1.9 ± 0.2 (4)[c]	1.7 ± 0.2 (3)[c]
$Cr(NH_3)_5(CN)^{2+}$	17[d]	16[d]		
$Cr(NH_3)_5(NCS)^{2+}$	0.25 ± 0.03 (3)[e]	0.20 ± 0.04 (3)[e]	0.26[f]	0.29[f]
$Cr(en)_3^{3+}$	1.6 ± 0.2 (5)[g]	1.6 ± 0.1 (5)[g]	1.6 ± 0.3 (3)[h]	1.5 ± 0.1 (2)[h]
trans-$Cr(en)_2F_2^+$			1.4 ± 0.2 (3)[i]	
$Cr(tn)_3^{3+}$	1.6 ± 0.1 (2)[j]	1.8 ± 0.2 (2)[j]		

[a] The conductivity lifetimes pertain to the second stage of the decrease in conductivity with the exception of *trans*-$Cr(en)_2F_2^+$, where only one change was detected. [b] Conditions: [Cr], 2.0 and 4.0 mM; λ(em), 645–665 nm; pH(cond), 2.5–3.1; pH(em), 2.6–3.1. [c] Conditions: [Cr], 3.0 and 4.0 mM; λ(em), 665 nm; pH(cond), 2.6–4.0; pH(em), natural pH and 2.7–4.0. [d] Conditions: [Cr], 2.5 mM; λ(em), 680 nm; pH, 3.1. [e] Conditions: [Cr], 2.0 mM; λ(em), 680 and 686 nm; pH(cond), 2.5–3.0 (H_2SO_4 and $HClO_4$); pH(em); 2.3–4.7 ($HClO_4$). [f] Conditions: [Cr], 1.6 mM; λ(em), 686 and 695 nm; pH, 2.7 ($HClO_4$). [g] Conditions: [Cr], 2.0–4.0 mM; λ(em), 670 nm; pH(cond), 2.3–3.1; pH(em), 2.6–3.1. [h] Conditions: [Cr], 2.0 and 4.0 mM; λ(em), 670 and 675 nm; pH, 2.3–3.2. [i] Conditions: [Cr], 0.24–0.63 mM; pH, 2.7–3.0 and 10.0–11.5. [j] Conditions: [Cr], 3.3 and 3.5 mM; λ(em), 660–680 nm; pH, 2.5 and 2.8.

Table III. Fraction of Conductivity Change Occurring with Same Lifetime as Emission in Acidic Media[a]

complex ion	fraction at 347-nm excitation	fraction at 530-nm excitation	comparative information from lit.[b]
$Cr(NH_3)_6^{3+}$	0.74 ± 0.04 (3)	0.80 ± 0.04 (5)	0.69 (B,Q),[c] ca. 0.5 (Q)[d]
$Cr(NH_3)_5(CN)^{2+}$	0.74 ± 0.04 (2)		0.73 (B, Q)[e]
$Cr(NH_3)_5(NCS)^{2+}$	0.77 ± 0.03 (3)	0.80	
$Cr(en)_3^{3+}$	0.67 ± 0.07 (2)	0.68 ± 0.06 (3)	0.70 ± 0.03 (A),[f] 0.38–0.58 (B),[g] 0.60 (Q)[h]
trans-$Cr(en)_2F_2^+$		1.0 (3)	
$Cr(tn)_3^{3+}$	0.78[i]		ca. 0.67 (B)[j]

[a] Unless otherwise noted, conditions were the same as those given in Table II. [b] Symbols: A, fraction for product formation as determined by time-resolved optical absorption measurement; B, fraction of chemical reaction quenched in basic media relative to yield in acidic solution; Q, fraction of chemical reaction quenched by agents other than hydroxide ion. [c] Aqueous Co(II).[20] [d] Ni(gly)$_2$.[30] [e] Cr(CN)$_6^{3-}$.[25] [f] Reference 27. [g] Extent of quenching remained relatively constant (ca. 0.5) for excitation wavelength between 436 and 502 nm but it decreased at 514 nm.[32] [h] Aqueous Co(II) and Fe(II).[33] [i] Conditions: [Cr], 3.3 mM; pH, 2.5. [j] Reference 38.

details of the results under the separate categories of acidic and alkaline solutions.

Acidic Media. The principal and general observation was that the conductivity not only decreased but it did so in two stages as exemplified in Figure 2. The sole exception to the two-stage sequence was *trans*-$Cr(en)_2F_2^+$, where only one change took place. These events began with the laser pulse, and depending on the specific complex, they continued over a period lasting upwards of 50 μs. No evidence for subsequent reactions was found in the longer time domains (ms–s scales) where looked for in the cases of $Cr(NH_3)_5(CN)^{2+}$, $Cr(NH_3)_5(NCS)^{2+}$, $Cr(en)_3^{3+}$, and $Cr(tn)_3^{3+}$.

Two procedures were employed to obtain the relevant kinetic time constants and the fractional changes in conductivity associated with the two stages. A double-exponential curve-fitting routine was used as described elsewhere.[26] On the basis of the observation that the rate of the first stage increased with increasing proton concentration whereas that of the second stage remained unaffected by changes in acidity, the two stages could be reasonably well resolved in time through control of pH. This permitted the longer term movement and the one involving the larger change in conductivity to be dealt with separately and its rate law to be determined as being first order. Computer-based extrapolation of this longer term component to the end of the laser pulse, as shown by the solid line in Figure 2a, also provided an additional means to measure the fractional changes in conductivity for the two stages. Both approaches gave agreement, and they showed that the rate laws for the first stage obeyed first-order kinetics.

Table II presents the lifetime for the conductivity change of the longer term process for each complex along with the measured emission lifetime. For the latter phenomenon, only one stage was observed, and in each instance, the rate law was

first order and independent of pH (and of excitation wavelength). The values of the emission lifetimes measured here are in good agreement with the reported ones (Table I). A comparison of the emission lifetimes with those for conductivity indicates that they are the same within experimental error and thus that the emission process is coupled mechanistically with the second reaction stage, independent of excitation wavelength.

The fraction of the overall conductivity change associated with the longer term process is summarized in Table III for each of the complex ions studied. Clearly this stage in each instance represents the bulk of the chemical reaction, between 67 and 80%, and for *trans*-$Cr(en)_2F_2^+$, 100%. Under our conditions, these fractional changes as well as lifetimes were in general independent of pH, complex concentration, and excitation wavelength (Table III). In contrast, the lifetimes for the first stage of the decrease in conductivity became smaller with increasing acid concentration.

The foregoing can be viewed in general terms as involving a two-stage sequence for the formation of photoproducts, followed by subsequent protonation of released ammonia or of the monodentate amine ligands. The lifetimes of the quartet levels, populated initially by 347- or 530-nm irradiation, are considered to be quite short for these types of complex ions.[5] For example, optical absorption studies for photoproduct formation from $Cr(en)_3^{3+}$ set an upper lifetime limit for the lowest quartet level ($^4T_{2g}$) at about 5 ns.[27] The observed values of τ for the first stage of decrease in conductivity for all of the systems studied were considerably longer than this. This indicates that protonation which occurs subsequently to photorelease of NH_3 or amine is rate determining during the *initial* stage. However, the experiments were designed through the control of pH to have the rate of exiting from the doublet state (second stage) be slow relative to that of protonation. The fact that lifetimes of the second stage, the fractional changes in conductivity, and the overall quantum yields of the products (as determined from steady-state photolysis experiments) are unaffected by changes in acidity demonstrates that the role

(50) pK_{a1}(H_2O) = 4.4, pK_{a2}(enH) = 8.8 for $Cr(en)_2(enH)(H_2O)^{4+}$.[51]
(51) Berg, T.; Jacobsen, J. *Acta Chem. Scand., Ser. A* **1975**, *A29*, 381.
(52) pK_a = 9.24 for NH_4^+.[53]
(53) Sillén, L. G.; Martell, A. E. *Spec. Publ.—Chem. Soc.* **1964**, *No. 17*, 150.

of protonation is not one involving inducement of excited-state chemical reactivity but is rather that of a scavenger for the resultant ground-state products.

In our preliminary report[26] on $Cr(en)_3^{3+}$, the observed first-order rate constant for the initial phase of the conductivity movement was found to be a linear function of proton concentration, yielding for both 347- and 530-nm excitation the same second-order rate constant of 3.6×10^9 M^{-1} s^{-1} for the reaction of the photoproduct:

$$Cr(en)_2(en)(H_2O)^{3+} + H^+ \rightarrow Cr(en)_2(enH)(H_2O)^{4+} \quad (1)$$
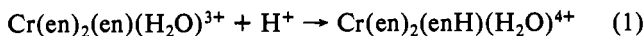
For $Cr(tn)_3^{3+}$, less extensive results suggest for the reaction analogous to eq 1 a value of about 5×10^9 M^{-1} s^{-1}. With *trans*-$Cr(en)_2F_2^+$, only one stage was observed, and here the rate was independent of pH. The latter is expected on the anticipation of the rate of protonation (eq 1) being faster than that for exiting from the excited state.[54]

For the three systems where the photosubstitution for ammonia is the predominant or sole process, the rates increased with proton concentration although it was not possible to discern if this was in fact a linear dependency because of the limits imposed by the time resolution of the apparatus. The measured lifetimes (and if pseudo first-order behavior is accepted: $[H^+] \gg [NH_3]$) suggest for all three complexes a second-order rate constant of $(1-2) \times 10^{10}$ M^{-1} s^{-1}, which is comparable to that of 4.3×10^{10} M^{-1} s^{-1} reported for the protonation of ammonia at ionic strengths (>0.1 M) higher than those used here (<0.03 M).[45]

An additional facet was that in two situations, irradiation at 347 nm for $Cr(NH_3)_5(NCS)^{2+}$ and at 530 nm for $Cr(en)_3^{3+}$, there occurred in near-coincidence with the laser pulse a very short duration increase in conductivity that took place prior to the subsequent decreases.[55] The nascent increase amounted to less than 30% of the overall change for $Cr(NH_3)_5(NCS)^{2+}$ and below 20% for $Cr(en)_3^{3+}$. Because of its very short duration, it was not feasible to study in detail its time dependence; however, at least in the case of $Cr(NH_3)_5(NCS)^{2+}$ for excitation at 347 nm, there are several features pointing to a possible chemical origin. The phenomenon was not observed for the other complexes or for $Cr(NH_3)_5(NCS)^{2+}$ at 530-nm excitation. Its magnitude was less pronounced with sulfuric acid (vs. perchloric acid), at higher proton concentrations and laser intensities, and with the sample prepared by us. Notwithstanding these aspects, the features associated with the subsequent decreases in conductivity (lifetimes and fractional changes in conductivity) were not affected.

Basic Media. A number of the foregoing complex ions was also investigated under alkaline conditions, where the situation for both the conductivity and the emission aspects was generally different from those observed in acidic solutions. With the exception of *trans*-$Cr(en)_2F_2^+$, the emission intensity progressively decreased with increasing pH, and concomitant with this, the lifetime became shorter. The decay of emission was first order, and the apparent rate constants were found to be a linear function of hydroxide ion concentration as exemplified in Figure 3. The second-order quenching constants, calculated from the slopes of such plots, are presented in Table IV. Our value of 7.7×10^9 M^{-1} s^{-1} for $Cr(NH_3)_5(CN)^{2+}$ at 347-nm excitation is comparable to that of 6.2×10^9 M^{-1} s^{-1} obtained for 530-nm excitation by others.[25] For the quenching studies, the upper pH limits were imposed by our ability to

(54) A preliminary study of the congeneric *trans*-$Cr(en)_2(NCS)_2^+$, where two conductivity stages are observed, suggests for the reaction corresponding to eq 1 a rate constant near 5×10^9 M^{-1} s^{-1}, and this implies a similar value for $Cr(en)(en)(H_2O)F_2^+$, where one of the en's is monodentate.

(55) The fractional changes in conductivity (Table III) were based on the difference between the maximum amplitude of the nascent increase and the long-term decrease in conductivity.
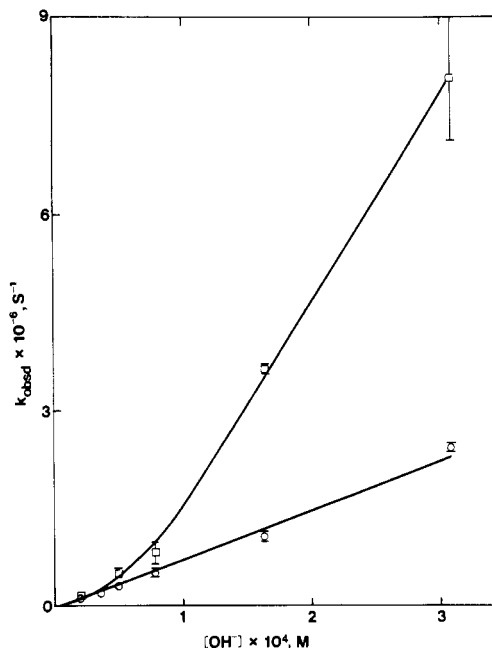
Figure 3. Plots of the observed first-order rate constants for quenching of emission at 680 nm (O) and for the decrease in conductivity (□) vs. concentration of hydroxide ion occurring on excitation of 2.5 mM $Cr(NH_3)_5(CN)^{2+}$ at 347 nm.

Table IV. Second-Order Rate Constants for Emission and Conductivity Changes in Basic Media

complex ion	emission lifetime quenching by OH$^-$			conductivity
	λ(excit), nm	λ(em), nm	$10^{-10}k$, M^{-1} s^{-1} a	$10^{-10}k$, M^{-1} s^{-1}
$Cr(NH_3)_6^{3+}$	530	665	2.3 ± 0.1	$4._1$ b
$Cr(NH_3)_5(CN)^{2+}$	347	680	0.77 ± 0.02	$2._5$ c
$Cr(NH_3)_5(NCS)^{2+}$	347	686	ca. 0.2	ca. 0.1 d
$Cr(en)_3^{3+}$	530	670	1.8 ± 0.9	$2._3$ e

a Determined from plots of k_{obsd} (s^{-1}) vs. $[OH^-]$; the pH range was natural pH to ca. 10.5. [Cr] ranged from 2.0 to 0.2 mM. b Calculated from observed rate constant ratio (cond/em) of $1.8 \pm 0.5/1$ at pH 10.2–10.5. c Calculated from observed rate constant ratio (cond/em) of $3.3 \pm 0.4/1$ at pH 10.2, 10.5. d Estimated from difference in k_{obsd}(cond) at pH 10.7 and 11.7. e Calculated from observed rate constant ratio (cond/em) of $1.3 \pm 0.3/1$ at pH 9.8.

detect the considerably reduced levels of emission as the pH was increased.

Conductivity experiments were performed generally at higher pH values because below about pH 10 the interferences from the partial protonation of ammonia and of the monodentate ligands introduced additional complexities.[46-53] Under these conditions of higher pH, the conductivity decreased and it did so, with the exception of $Cr(NH_3)_5(NCS)^{2+}$, in one stage as illustrated in Figure 2c. The rate law for this stage appeared to be first order for a given pH. The associated rate constants increased in value as the pH of the solutions was raised; however, the plots of the observed rate constant vs. concentration of hydroxide ion did exhibit some upward curvature. The most prominent example for this occurred for $Cr(NH_3)_5(CN)^{2+}$ as shown in Figure 3. In the higher pH region, such plots are nearly linear, and with use of the ratios of the observed rate constants for the conductivity change relative to those for the corresponding emission, estimates have been made for the second-order rate constants. These are given in Table IV. Although these numerical values should be treated with some caution (see below), it was quite clear that, in the cases of $Cr(NH_3)_6^{3+}$ and $Cr(NH_3)_5(CN)^{2+}$, the rates for the decrease in conductivity *exceeded* those for the quenching of

emission, whereas with $Cr(NH_3)_5(NCS)^{2+}$ and $Cr(en)_3^{3+}$ they were nearly the same.

No further change in conductivity (up to 1 s after the laser flash) was observed for $Cr(NH_3)_6^{3+}$, $Cr(NH_3)_5(CN)^{2+}$, and $Cr(en)_3^{3+}$. For these systems, we also undertook a comparison of the overall conductivity movement in basic media (pH $\gtrsim 11$) relative to that in acidic solutions. This was done under conditions where the conductances of the two solutions were at comparable levels so as to ensure that the signal response of the apparatus was the same. The results of these experiments are summarized in Table V, and they show in each instance that the ratio of the single change in basic media to that of the first stage encountered in acidic solution was essentially 1:1. Under these highly basic conditions, the emission was effectively quenched.

Similar studies for $Cr(NH_3)_5(NCS)^{2+}$ were not feasible to carry out because hydroxide ion was found to be a less effective agent for emission quenching and conductivity change (Table IV), coupled with a lower emission quantum yield[22] and shorter intrinsic lifetime for this complex ion. An additional facet was that, at the highest pH used (pH 11.7, 347-nm excitation), there appeared to occur two stages to the decrease in conductivity whereas at a lower pH of 10.7 only one stage was apparent. The faster component and the one associated with the rate constant given in Table IV accounted for about 75% of the overall conductance change. The second and lesser component exhibited a rate of about a factor of 5 slower than that of the first one. Studies at even higher pH were precluded by instrumentation response and possible thermal instability of the complex.

In contrast to the behavior of the complexes described above, that of *trans*-$Cr(en)_2F_2^+$ was remarkably different in that, in basic and acidic solutions, a single stage of decrease in conductivity was found and the lifetimes were the same within experimental error over the pH ranges of 2.7–3.0 and 10.0–11.5. The ratio of the change in conductance in alkaline media to that in acidic solution is given in Table V. In the pulsed-laser experiments, the emission was not detectable probably due to its low quantum yield and broad spectrum.[22] Therefore, the emission intensities of degassed solutions at pH 3.0 and 11.0 were measured under steady-state conditions for 510-nm excitation,[56] and this comparison gave no indication of any quenching of emission in basic media. The foregoing results suggest that the rate constant for quenching by hydroxide ion is less than 10^8 M^{-1} s^{-1}.

Discussion

Role of Excited States. The results obtained in acidic media focus attention on two prominent and interrelated features: the formation of the photoaquation products occurring in two distinct stages (the sole exception being the fluoro complex) and the longer term but major component having the same lifetime as that for emission (Tables II and III). The faster and relatively minor initial stage reflects prompt formation of product(s). The time scales for these events are undoubtedly short (nanosecond or subnanosecond),[5,27,57] although as explained above the actual conductivity processes being monitored were the subsequent, slower ones for protonation of the released NH_3 and of the monodentate ethylenediamine and propanediamine ligands. Since these last rates exceeded those for the decay of emission from the doublet state(s), the clear implication is that the origins of the promptly formed products reside in very short-lived quartet states. The fact that, for $Cr(NH_3)_6^{3+}$, $Cr(NH_3)_5(CN)^{2+}$, and $Cr(en)_3^{3+}$, the fractional changes in conductivity were the same within experimental error for irradiation of both the L_1 and the L_2 quartet bands

seems to indicate that there is no chemical reaction from the higher quartet levels and perforce the lower quartet states are the chemically reactive ones. This is in keeping with the observation that the overall chemical yields are relatively independent of excitation wavelength in these regions (Table I). An additional event in the case of $Cr(NH_3)_5(NCS)^{2+}$ was a nascent increase in conductivity for 347-nm excitation. Prompt release of NCS^- can contribute to such an increase; however, this is not the sole explanation for it because no significant increase occurred for excitation at 530 nm whereas the overall yields of NCS^- are comparable but small for the two regions near 347 and 530 nm (Table I). One possible explanation to account for the change being an increase in conductivity could be the presence of a photohydration reaction to yield a proton and a species such as $Cr(NH_3)_5(NCSOH)^+$; however, further investigations under conditions of time resolution much shorter than those available here are needed to discern if this is so. In any event, the occurrence of this phenomenon had no apparent effect on the levels of the subsequent and major decreases in conductivity.

The principal conductivity changes for all of the systems studied occurred in concert with the emission decays. In Table III, the fractional changes in chemical reaction for this stage are compared with results from steady-state experiments for the quenchable portion of reaction and with a time-resolved optical absorption measurement of product formation in the case of $Cr(en)_3^{3+}$ (eq 1). In general, the agreement is quite satisfactory, particularly in consideration that the results have been obtained from different types of procedures and conditions. This combination of evidence clearly underscores the dominant role that passage through the doublet state(s) plays in the sequence of photochemical events.

Considerable interest is currently focused on whether chemical reaction occurs directly from the doublet level or indirectly via thermal back intersystem crossing (bisc) to the lowest quartet state(s) followed by chemical change (or some combination thereof). In the case of $Cr(NH_3)_5(NCS)^{2+}$, our findings in conjunction with those of earlier reports now provide a basis for concluding that bisc may play a prominent role in the photosubstitution of ammonia. The evidence to be considered is as follows. Ammonia aquation is the dominant process, and the steady-state quantum yields are relatively constant over the range of 373–546 nm (Table I) although $\Phi(NH_3)$ drops to about one-third of its former values for irradiation in the doublet region (652 nm).[17,37] The ratios of $\Phi(NH_3)/\Phi(NCS)$ for wavelengths closest to our excitation positions are 15.5/1 (373 nm) and 21/1 (546 nm), but the ratio decreases to 8.2/1 for doublet irradiation: The drop is primarily due to the decrease in $\Phi(NH_3)$. Our finding is that 80% of the conductivity change, which is a *decrease* representing consumption of proton by reaction with NH_3, transpires with the same rate as that for emission from the doublet state. That the conductivity changes reflect predominantly ammonia release is readily recognized by the realization that $\Phi(NH_3)$ is substantially greater than $\Phi(NCS)$ and that the situation is further biased toward NH_3 detection by virtue of the equivalent ionic conductivity of proton being markedly larger than that for NCS^-. Martin and Adamson[36] found in steady-state photosensitization with acridine a very significant increase in the ratio of $\Phi(NH_3)/\Phi(NCS)$ (33/1). This finding in association with the results for direct photolysis cited above led them to conclude that the doublet-state chemistry is entirely one of NCS^- aquation and that of the first excited quartet state is largely one of NH_3 aquation. This latter aspect can now be extended to include bisc from the doublet to a low-lying quartet state as about 80% of the ammonia aquation occurs in connection with the decay of the doublet-state emission, and if it is assumed that the photosensitization results do not reflect

(56) Oka, T.; Knight, A. R.; Steer, R. P. *J. Chem. Phys.* **1977**, *66*, 699.
(57) Castelli, F.; Forster, L. S. *J. Phys. Chem.* **1977**, *81*, 403.

modification to the photochemical processes.

In the case of *trans*-Cr(en)$_2$F$_2^+$, only one stage of conductivity change is observed, and the associated lifetime agrees with that reported for the decay of emission (Table II).[10] While the results of an earlier study based on time-resolved absorption detection of product formation had suggested about 75% of the chemical reaction occurring in conjunction with emission,[5] more recent results from steady-state quenching experiments corroborate the conductivity finding.[14] We conclude that one state is predominantly responsible for the photoreactivity. This state appears to be of doublet character on the basis of the emission assignment made by Flint and Matthews[58,59] and the correspondence between the conductivity and emission lifetimes. Of note here is that the parentage of the emitting state ($^2E_g(D_{4h})/^2T_{1g}(O_h)$)[58] for *trans*-Cr(en)$_2F_2^+$ is different from those of systems such as Cr(NH$_3$)$_6^{3+}$ (^2E_g-(O_h)).[60] This feature may potentially be a factor in determining the relative sensitivities of doublet-state species toward quenching by hydroxide ion.

For the Cr(en)$_3^{3+}$ and Cr(NH$_3$)$_5$(CN)$^{2+}$ cases, the presence of two reaction stages and the occurrence of isomeric products (Table I) provide additional facets to be considered. Because the pK_a values for the isomers are known or expected to be nearly the same,[48,49] our conductivity results will not distinguish between their formations. Notwithstanding this qualification, it is notable for both complexes that the ratios of the isomeric quantum yields are independent of excitation wavelength (including the doublet region for Cr(en)$_3^{3+}$). Since the formation of the same isomeric ratio for both the doublet and quartet levels is rather improbable,[3,18] one possible explanation is that the photoreactions are state specific but with rapid interconversion between states; i.e., stationary or equilibrium conditions apply. Alternatively the constancy of the ratios with wavelength may reflect nearly exclusive reaction through low-lying quartet levels, involving in part bisc albeit to one or more levels.
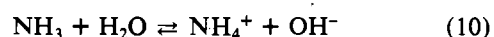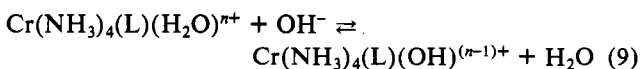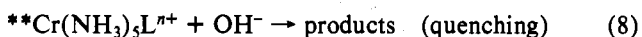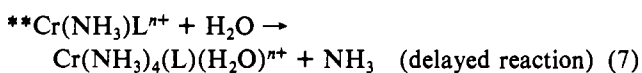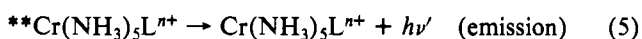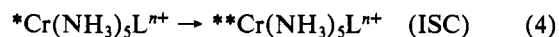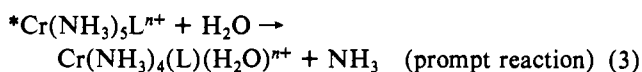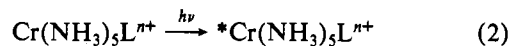
These types of mechanisms do not, however, appear to be entirely satisfactory, partly because they tend to focus on explaining events in the thexi-state time domains whereas other aspects allude also to the chemical importance of the earlier processes. The occurrence of generally two reaction periods with the fractional changes being independent of wavelength (Table III) clearly indicates similar responses, following excitation, in *both* the shorter and longer term time frames, and ones that are highly specific for systems exhibiting nontrivial chemical yields. In this regard, it is observed for Cr-(NH)$_5$(CN)$^{2+}$ that reaction quenching by OH$^-$ at the doublet level which does not induce further chemical change (see belov), gives the same isomeric ratio as that in the absence of quenching.[25] While back intersystem crossing could be involved here (in the manner of the Cr(NH$_3$)$_5$(NCS)$^{2+}$ case), the remarkable feature is that the isomeric ratio is the same for both the prompt and longer term stages of reaction. The concept, recently expressed by Hollebone, Langford, and Serpone concerning states decaying along a specific nuclear coordinate(s) (DOSENC model),[3] appears more in keeping with the above findings. This aspect can be viewed in conjunction with the suggestion of Kane-Maguire, Richardson, and Toney[31] that through spin–orbit coupling and under lowered symmetry for the excited states mixing of the doublet and quartet levels transpires to yield a single energy surface with the thexi states representing potential energy minima.[61] In

this context, back intersystem crossing loses something of its original meaning; however, the idea of thermally activated motion between the various minima regions remains valid.

Quenching Processes in Basic Media. For Cr(NH$_3$)$_6^{3+}$, Cr(NH$_3$)$_5$(CN)$^{2+}$, Cr(NH$_3$)$_5$(NCS)$^{2+}$, and Cr(en)$_3^{3+}$, both the emission intensities and the lifetimes decrease with increasing hydroxide ion concentration. The rate constants associated with quenching of the lifetimes are given in Table IV. Under our conditions, the quenching is probably dynamic in type rather than static because the latter seems improbable. On the basis of the reported formation constant for the Cr-(en)$_3^{3+}$·OH$^-$ ion pair,[62] an upper limit to the fraction of ion pairing here is estimated to be less than 3%. The absence of ion pairing is corroborated by the UV spectral results for Cr(en)$_3^{3+}$ solutions at pH 10.6, although Kane-Maguire and co-workers did find evidence for such formation at much higher alkalinity (0.05 M OH$^-$).[32] The situation for Cr(NH$_3$)$_6^{3+}$ appears comparable, and for the lowered charged complex ions, the likelihood of static quenching seems even less probable. The dynamic nature is consistent with the values of the quenching rate constants being at a level near those for diffusion-controlled processes.

Associated with the emission changes, there occurred alterations to the decreases in conductivity, which reflect in part a net consumption of hydroxide ion. The fact that the observed first-order rate constants for conductivity exceeded or were nearly the same as those for emission quenching and that the ratios of the conductance change at high pH relative to the first stage of decrease in acidic media are essentially 1/1 (Table V) provides additional support for a prompt component to chemical reaction.

The observation of some upward curvature to the plots of the apparent first-order rate constants for changes in conductivity as a function of hydroxide ion concentration (Figure 3) indicates contributions from more than one process at least in the less basic solutions.[63] Reactions 2–10 serve to exemplify the situation, with L being ammonia or cyanide and the single and double asterisks designating electronically excited quartet and doublet species, respectively.

$$Cr(NH_3)_5L^{n+} \xrightarrow{h\nu} {}^*Cr(NH_3)_5L^{n+} \qquad (2)$$

$$^*Cr(NH_3)_5L^{n+} + H_2O \rightarrow$$
$$Cr(NH_3)_4(L)(H_2O)^{n+} + NH_3 \quad \text{(prompt reaction)} \quad (3)$$

$$^*Cr(NH_3)_5L^{n+} \rightarrow {}^{**}Cr(NH_3)_5L^{n+} \quad \text{(ISC)} \qquad (4)$$

$$^{**}Cr(NH_3)_5L^{n+} \rightarrow Cr(NH_3)_5L^{n+} + h\nu' \quad \text{(emission)} \qquad (5)$$

$$^{**}Cr(NH_3)_5L^{n+} \rightarrow Cr(NH_3)_5L^{n+} \quad \text{(ISC)} \qquad (6)$$

$$^{**}Cr(NH_3)L^{n+} + H_2O \rightarrow$$
$$Cr(NH_3)_4(L)(H_2O)^{n+} + NH_3 \quad \text{(delayed reaction)} \quad (7)$$

$$^{**}Cr(NH_3)_5L^{n+} + OH^- \rightarrow \text{products} \quad \text{(quenching)} \qquad (8)$$

$$Cr(NH_3)_4(L)(H_2O)^{n+} + OH^- \rightleftharpoons$$
$$Cr(NH_3)_4(L)(OH)^{(n-1)+} + H_2O \quad (9)$$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad (10)$$

For Cr(en)$_3^{3+}$, there will be reactions corresponding to eq 9 and to eq 11. Reactions 2–7 do not contribute directly to

$$Cr(en)_2(en)(OH)^{2+} + H_2O \rightleftharpoons$$
$$Cr(en)_2(enH)(OH)^{3+} + OH^- \quad (11)$$
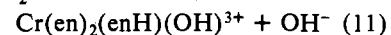
changes in conductance; however, they will influence the time evolution of such changes. Both eq 9 and eq 10 (or 11) directly

(58) Flint, C. D.; Matthews, A. P. *J. Chem. Soc., Faraday Trans. 2* **1974**, 70, 1307.

(59) Dr. A. D. Kirk kindly drew our attention to ref 58 and indicated that the assignment of the emission of delayed fluorescence (ref 5 and 22) is considered to be in error.

(60) Flint, C. D.; Greenough, P.; Matthews, A. P. *J. Chem. Soc., Faraday Trans. 2* **1973**, 69, 23.

(61) Wilson, R. B.; Solomon, E. I. *Inorg. Chem.* **1978**, 17, 1729.

(62) Beck, M. T. *Coord. Chem. Rev.* **1968**, 3, 91.

(63) Under the conditions used here, the shift in the autoionization reaction of water will occur at a rate comparable to or exceeding those observed.

Table V. Ratio of Conductivity Change in Basic Media to Prompt Change in Acidic Media[a]

	$\Delta\Lambda$(base)/$\Delta\Lambda$(acid)		
complex ion	347-nm excitation	530-nm excitation	predicted ratio[b]
$Cr(NH_3)_6{}^{3+}$	1.1 ± 0.3^c	0.8 ± 0.2^d	ca. 1.3
$Cr(NH_3)_5(CN)^{2+}$	1.0 ± 0.2^d		ca. 1.2
$Cr(en)_3{}^{3+}$	1.0 ± 0.3^e	0.8 ± 0.1^f	ca. 1.0
trans-$Cr(en)_2F_2{}^+$		0.8 ± 0.1^g	ca. 0.9

^{a} [Cr] ranged from 0.1 to 3.0 mM, and it was the same for acidic and basic solutions of a given complex. The pH was adjusted by addition of $HClO_4$ and of NaOH so that conductances of acidic and basic media were approximately the same. ^{b} Ratio predicated on reactivity of OH^- not inducing excited-state chemical reaction; see text. ^{c} pH 11.3, pH 2.9. ^{d} pH 11.2, pH 3.0. ^{e} pH 11.7, pH 2.6. ^{f} pH 11.7, pH 2.6. ^{g} pH 11.0 and 11.5, pH 2.7 and 3.0.

affect the conductance level but in opposing directions.[64] Above about pH 10, the reaction of eq 10 will not contribute significantly to the conductivity because the position of equilibrium lies well to the left whereas that of eq 9 is a major factor at all basic pHs.[46-53] Furthermore, the reactant $Cr(NH_3)_4(L)(H_2O)^{n+}$ of eq 9 is formed via two separate steps (eq 3 and 7) with the latter one being in competition with those of eq 5-8. Equation 7 can reflect back intersystem crossing followed by prompt chemical reaction and/or direct reaction from the doublet.

Of immediate interest is whether or not the quenching process (eq 8) induces further net chemical change, and the information in Table V is pertinent to this point. For pH >11, quenching of emission is essentially complete and only one conductivity step is apparent. The overall level of conductivity change here is approximately the same as that of the first stage of decreasing conductivity taking place in acidic solutions that is accounted for by eq 3 followed by

$$NH_3 + H^+ \rightarrow NH_4{}^+ \qquad (12)$$
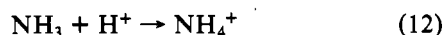
Included in Table V are predicted ratios, based on $\Delta\Lambda$(acid) being derived from eq 3 and 12 and $\Delta\Lambda$(base) reflecting only eq 3 and 9, i.e., assuming eq 8 (quenching) does not lead to net chemical change. The values of $\Delta\Lambda$ were calculated from known or estimated equivalent ionic conductivities for the ions involved.[65-67] The observed and predicted ratios are in reasonable agreement: If the somewhat lower observed values for 530-nm excitation suggest any trend, it is toward less amount of change in basic media than that expected. We conclude on an operational basis that, for $Cr(NH_3)_6{}^{3+}$, $Cr(NH_3)_5(CN)^{2+}$, and $Cr(en)_3{}^{3+}$, quenching (eq 8) does not induce net chemical reaction, and this is also consistent with the results of steady-state, chemical quenching experiments (Table III). Our findings also support the conclusions that at the levels of hydroxide ion used here, this agent was not influencing events from the upper states and that the second-order rate constants given in Table IV for conductivity pertain predominantly to the forward reactions of eq 9. These

values in conjunction with the pK_a values for the aquo complexes imply that the rate constants for the reverse reactions of eq 9 are about 100 s^{-1}.

While, in these circumstances, hydroxide ion is functioning in an operational sense as an "innocent" type of quenching agent, several possible mechanisms could account for this. Kühn and co-workers[21] find that the radiationless transition rate from the doublet to the ground state in chromium(III) amine complexes correlates with the number of N–H bonds, and the proximity of OH^- may consequently enhance the nonradiative rates. A chemical viewpoint proposed by Langford and Tipping invokes deactivation via proton transfer to form an amido species such as $Cr(NH_3)_5(NH_2)^{2+}$.[35] Our results do not rule out this latter mechanism because the ground-state reprotonation of the amido ligand could well be so fast as to go undetected here: The pK_b values are likely to be less than 1, implying the possibility of very rapid forward rates.[32] In this context, it is pertinent to recognize that hydroxide ion quenching of the photobehavior for trans-$Cr(en)_2(NCS)_2{}^+$ appears to be of chemical origin but the mechanism is yet to be identified[30] and that there is an indication of possible noninnocent behavior in our observations on $Cr(NH_3)_5(NCS)^{2+}$ at pH 11.7. On the other hand, hydroxide ion is not a particularly effective quenching agent for trans-$Cr(en)_2F_2{}^+$ or for $Cr(bpy)_3{}^{3+}$.[4,39]

The degree to which a particular agent such as OH^- is judged to be innocent or noninnocent appears to vary even between seemingly similar complex ions as illustrated above. Furthermore, for a given complex, conditions can play a vital role as the quenching agent has the potential capability to affect a variety of important factors such as intersystem crossing, differences in levels of reactivity for various excited states, and geminate recombination.[4,5,11,33,68] Such factors may be reflected in the difference, particularly in the 500-nm excitation region for $Cr(en)_3{}^{3+}$, between our findings and the lower degree of reaction quenching found by Kane-Maguire and co-workers[32] in steady-state experiments performed at hydroxide ion concentrations (0.01–0.1 M) higher than those used here (Table III[69]). By contrast, the quenching results obtained by Krause and Wasgestian[20] for $Cr(NH_3)_6{}^{3+}$ at 0.1 M OH are in closer accord with our results as are also those for $Cr(NH_3)_5(CN)^{2+}$.[25] Clearly results from both steady-state types of experiments and time-resolved ones such as performed here are needed in order to better understand the roles of quenching agents and in particular the OH^- that is an intimate member of the solvent system.

(64) At pH $\gtrsim$10, the concentration of OH^- will have been greater than those of the photoproducts whereas at near pH 9 this may not have been the case. This situation may have contributed to changes in k_{obsd}(cond) with pH.

(65) Takahashi, T.; Koiso, T. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2784.

(66) Riccieri, P.; Zinato, E. *Inorg. Chem.* **1980**, *19*, 853.

(67) "Landolt-Börnstein, Zahlenwerte und Functionen", 6th ed.; Springer-Verlag: Berlin, 1960; Vol. II, Part 7, pp 259–260.

(68) Conti, C.; Castelli, F.; Forster, L. S. *Inorg. Chim. Acta* **1979**, *33*, L171.

(69) Kirk, A. D.; Namasivayan, C. *Inorg. Chem.* **1983**, *22*, 2961.