Inorg. Chem. **1980**, *19*, 445–447

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Photolysis of *cis*- and *trans*-Dicyanobis(ethylenediamine)chromium(III) Ions

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Received June 7, 1979

The photochemical aquation of *cis*- and *trans*-dicyanobis(ethylenediamine)chromium(III) ions has been studied in acidic aqueous solution. The trans complex has one reaction mode in which proton uptake is observed, but essentially no cyanide is released. This is taken to represent release and protonation of one end of an en ligand, with a quantum yield of 0.6. The cis complex also releases en in a one-ended mode with $\Phi = 0.4$, and, in addition, cyanide loss is observed, with $\Phi = 0.1$. The results are dicussed in terms of current theories of photochemical reaction mode.

Introduction

The development of theoretical interpretions of the photochemistry of chromium(III) complexes was initiated and stimulated by the formulation of Adamson's rules[1] which set up a predictive model for photolabilization of specific ligands. Linck et al.[2] and Wrighton, Gray, and Hammond[3] have extended this model by including σ- and π-bonding strength effects and the consideration of reaction mode predictions for various excited states. Zink has extended his original ligand field theory[4] to an extended Hückel MO calculation to predict relative labilization of different ligands for complexes with less than O_h symmetry.[5] More recently, Vanquickenborne and Ceulemans[6] have presented a more accessible ligand field model to calculate relative bond energies of the different ligands in the excited states of near octahedral d^3 and d^6 complexes and thus to predict the mode of lability.

Until Pyke and Linck's[2] studies on *trans*-$\mathrm{Cr(en)_2F_2}^+$, all of the experimental data were consistent with Adamson's rules: the axis of labilization is that with the weakest ligand field and the leaving ligand on that axis is that having the stronger ligand field. Since en is the photolabile ligand in the trans-difluoro complex and therefore is an exception to Adamson's rules, Pyke and Linck[2] suggested σ bonding as a more appropriate criterion of lability than overall ligand field strength.

In consideration of the role of π bonding in determing ligand photolability, it is appropriate to investigate complexes with ligands for which there is considerable variation in π-donor and -acceptor ability.[6,7] An important ligand yet to be investigated in juxtaposition with others is cyanide; so far only $\mathrm{Cr(CN)_6}^{3-}$ has been investigated photochemically.[8] Recent reports[9,10] of synthesis of *cis*- and *trans*-$\mathrm{Cr(en)_2(CN)_2}^+$ provide an opportunity for a further test and extension of the range of validity of the various models and theories for photolabilization. We present here the results of our investigation of the photochemistry of these complexes.

Experimental Section

cis- and *trans*-$\mathrm{[Cr(en)_2(CN)_2](ClO_4)}$ were prepared by the method of Kaizaki, Hidaka, and Shimura[9], but, in our hands, the method did not give consistent results. In fact, on most attempts, no recoverable dicyano complex was obtained. The cis complex could be made by the alternate literature procedure[10] or, more easily, by either of two further methods, which we explored to try to improve the trans yield: (i) addition of the stoichiometric amount of KCN to *trans*-$\mathrm{[Cr(en)_2Br_2]Br}$ in DMF with reaction overnight at 35–40 °C and (ii) reaction of chromium trichloride hexahydrate plus the stoichiometric amount of KCN in methanol under reflux, with a stoichiometric amount of ethylenediamine added slowly over a 1-h period. From the fact that only the cis product was obtained from these preparations as with the method of Sattelberger, Darsow, and Schaap,[10] we tentatively conclude that unless the reaction can be carried out at or below room temperature, no trans complex will be formed.

The limited amount of the trans compound available to us became a major obstacle to our subsequent studies of the thermal and photochemical reactions.

The complexes were separated and purified by ion-exchange chromatography on a 30 cm × 25 cm ϕ column of Dowex 50W-X8 resin, 100 mesh, eluted with 0.5 M $\mathrm{LiClO_4}$, with subsequent isolation as described by Kaizaki et al.[9] The visible spectra and their extinction coefficients (cis 434 (69.5), 339 (62.2); trans 433 (50.1), 337 (42.7)) agree with those in the literature[9,10] as do the infrared spectra.

Photolyses were carried out in a thermostated 1 cm × 1 cm spectrophotometer cell. Samples were irradiated with a 1000-W AH6 mercury lamp through appropriate Corning glass filters for 366 nm or Balzers interference filters for 436 nm. The incident intensity was continuously monitored by reflecting about 8% of the collimated beam out to an RCA 935 phototube. The latter was calibrated frequently against the ferrioxalate actinometer.

Analysis for pH change was by means of a Metrohm combination microelectrode and a Metrohm Compensator pH meter reading to 0.001 pH unit.

Analysis for free cyanide required the prior removal of the cyanide-containing complexes. Of several analytical procedures tried, the most satisfactory was based on a picrate colorimetric method.[11] Immediately after photolysis, the sample solution was made basic with a few drops of dilute NaOH solution, pipetted onto a 7 × 5 mm column of Hamilton HA-X8.00 anionic exchange resin, and washed with pH 12 NaOH solution, all in the dark. The free cyanide retained by the column was then eluted with slightly acid 1 M NaCl solution into a 10 mL volumetric flask containing 1 mL of 5% $\mathrm{Na_2CO_3}$ and 5 mL of 1% picric acid solution. After the sample was heated on a steam bath for 20 min, it was cooled and made up to volume. The absorbance at 520 nm was determined and compared with calibrations.

The analytical method was tested by addition of a standard amount of cyanide to an unphotolyzed sample of complex and comparison of proton uptake at pH 3 with the cyanide analysis. In such a calibration experiment, two successive 1.00 μmol samples of KCN were added, without significant dilution effects, to 2.3 mL of a solution containing 2.0×10^{-3} M $\mathrm{HClO_4}$ and 8.4×10^{-3} M *cis*-$\mathrm{[Cr(en)_2(CN)_2](ClO_4)}$. The successive ΔpH values observed were 0.115 and 0.148. Since

$$\Delta[\mathrm{H}^+] = [\mathrm{H}^+]_0(1 - 10^{-\Delta\mathrm{pH}}) \qquad (1)$$

the proton uptakes were 1.07 and 1.02 μmol, respectively. Direct

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(1) Adamson, A. W. *J. Phys. Chem.* **1967**, *71*, 798.
(2) Pyke, S. C.; Linck, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 5281.
(3) Wrighton, M.; Gray, H. B.; Hammond, G. S. *Mol. Photochem.* **1973**, *5*, 165.
(4) Zink, J. I. *J. Am. Chem. Soc.* **1972**, *94*, 8039; *Mol. Photochem.* **1973**, *5*, 151; *Inorg. Chem.* **1973**, *12*, 1957.
(5) Zink, J. I. *J. Am. Chem. Soc.* **1974**, *96*, 4464.
(6) Vanquickenborne, L. G.; Ceulemans, A. *J. Am. Chem. Soc.* **1977**, *99*, 2208; *Ibid.* **1974**, *96*, 4464.
(7) Perumareddi, J. R. *Coord. Chem. Rev.* **1969**, *4*, 73.
(8) Chiang, A.; Adamson, A. W. *J. Phys. Chem.* **1968**, *72*, 3827.
(9) Kaizaki, S.; Hidaka, J.; Shimura, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 902.
(10) Sattelberger, A. P.; Darsow, D. D.; Schaap, W. B. *Inorg. Chem.* **1976**, *15*, 1412.
(11) Snell, F. D.; Snell, C. T. "Colorimetric Methods of Analysis", 3rd. Ed.; Van Nostrand: New York, 1949; Vol. III, p 864.

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Table I. Quantum Yields of Proton Uptake (Φ_{H^+}) and of Cyanide Ion (Φ_{CN^-}) in the Photolysis of *cis*- and *trans*-$Cr(en)_2(CN)_2^+$ in Aqueous Acid Solution

complex	λ_{ex}, nm	Φ_{H^+}	Φ_{CN^-}
cis-$Cr(en)_2(CN)_2^+$	436	0.51 ± 0.04 (9)	0.088 ± 0.005 (3)
	366	0.45 ± 0.05 (4)	0.104 ± 0.026 (3)
trans-$Cr(en)_2(CN)_2^+$	436	0.58 ± 0.10 (3)	0.02 ± 0.02 (1)
	366		0.05 ± 0.05 (1)

cyanide analysis by the above procedure gave 1.96 μmol for the total free cyanide.

Since the pH was monitored in situ before, during, and after the run and since photolysis lasted less than 2 min, correction of proton uptake for pH electrode equilibration and drift, and the thermal decomposition of the sample presented no problems. For the cyanide yield, the duration of the run included the dissolution of the sample, thermal equilibration, the photolysis itself, and the chromatographic isolation of free cyanide. Further, cyanide is retained by the anion resin only if the sample and wash are basic, pH >11. Our data indicate that some additional decomposition on the resin occurs, likely involving the protonated one-ended ethylenediamine complex releasing additional cyanide. Only those runs carried out as rapidly as possible give reliable results; more leisurely experiments, e.g., in which pH change was followed, invariably gave high and erratic cyanide analyses.

Results

Both *cis*- and *trans*-$Cr(en)_2(CN)_2^+$ were observed to aquate thermally at significant rates, the trans being the less stable. For the purpose of applying thermal corrections to the photochemical data, rough estimates of the rate constants were measured under the photolysis conditions. The trans isomer gave a proton uptake rate constant of about $4 \times 10^{-5}\ s^{-1}$, of which 25% represented cyanide released. The cis isomer yielded an overall rate constant of about $2 \times 10^{-5}\ s^{-1}$.

Photolysis of *cis*- and *trans*-$Cr(en)_2(CN)_2^+$ was studied with 366- and 436-nm excitation at 12–14 °C. Initially, $[H^+] = 2.0 \times 10^{-3}$ M, and concentrations of the complexes were in the range of $(0.6–1.2) \times 10^{-2}$ M for the cis and $(1.2–1.5) \times 10^{-2}$ M for the trans. Photolyses were limited to less than 10% conversion, and corrections were applied for thermal decomposition. Incident intensities were about 4×10^{-8} einstein s^{-1} at 436 nm and 2.5×10^{-8} einstein s^{-1} at 366 nm.

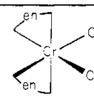
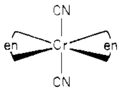
The quantum yields for proton uptake and for cyanide release, with the number of runs in parentheses, are given in Table I. The error limits given in Table I are the standard deviations of each data set except for the cyanide yields for the trans complex. There only one run was possible at each wavelength so the error given is an estimate based on the experimental uncertainties.

Discussion

For *trans*-$Cr(en)_2(CN)_2^+$, the simple ligand field theory calculation of the energy levels of the split $^4T_2$ state places the $^4B_2$ component 2530 cm^{-1} below the ^4E state, an ordering unique among trans-diacido Cr(III) complexes so far studied photochemically. There is, however, no evidence in the absorption spectrum for this splitting, a situation paralleling that of *trans*-$Cr(en)_2(NCS)_2^+$ ion.[12]

Table II shows the predictions based on the theory of Vanquickenborne and Ceulemans[6] for the bond energies of Cr–en and Cr–CN in the $^4B_2$ and ^4E excited states. If all internal conversion processes within the excited quartet manifold occur so rapidly that only the $^4B_2$ can be involved in the photoreaction, the theory predicts loss of ethylenediamine only (loss of one end of the chelated ligand with simultaneous protonation of the free end, as is generally the case for en complexes[13]). This is in accord with the experimental results that labilization is almost exclusively ethylenediamine for the trans complex.

Table II. Excited State Bond Energies I^*(Cr–L) Predicted by Vanquickenborne and Ceulemans'[6] Model (cm^{-1})

bond (axis)	I^*	excited state	bond (axis)	I^*	excited state
cis-$Cr(en)_2(CN)_2^+$ $^4B_2-^4E(^4T_2) = 1265\ cm^{-1}$					
Cr–en (ax)	8 580	^4E	Cr–en (eq)	11 870	^4E
Cr–en (eq)	8 975	$^4B_2$	Cr–en (ax)	14 360	$^4B_2$
Cr–CN (eq)	10 890	$^4B_2$	Cr–CN (eq)	14 450	^4E
trans-$Cr(en)_2(CN)_2^+$ $^4E(^4T_2)-^4B_2 = 2530\ cm^{-1}$					
Cr–en (eq)	8 975	$^4B_2$	Cr–CN (ax)	11 932	^4E
Cr–en (eq)	11 230	^4E	Cr–CN (ax)	17 540	$^4B_2$

Although Vanquickenborne and Ceulemans[6] caution that their theory is intended to apply only to the lower energy component of the first excited quartet state, we feel an extension to other states is warranted provided the appropriate photophysical processes connecting the states with the lower energy component are considered. For example, in the ^4E state of the trans complex, the bond energies of Cr(III) with en and with CN^- differ by only 700 cm^{-1}, so that if the ^4E state were involved in the photochemistry, some CN^- labilization might be expected. That this is not so to any appreciable extent implies no role for the ^4E state in the excited state processes. It lies about $12kT$ above the $^4B_2$ state, so that its equilibrium concentration at room temperature relative to the $^4B_2$ state would be extremely small. Irradiation at the wavelengths used in our experiments populates both split components of the ^4T state (436 nm) and the $^4E(^4T_1)$ (366 nm). The near complete absence of CN^- labilization implies that internal conversion of the two ^4E states to $^4B_2$ is too rapid for photochemical reaction to compete.

The *cis*-$Cr(en)_2(CN)_2^+$ ion has the inverse order of excited states, based on en–en as the unique axis (see Table II). Of the two components of the $^4T_2$ state, the ^4E is the lower in energy, lying 1260 cm^{-1} lower than the $^4B_2$ state. Again, there is no evidence for the splitting in the absorption spectrum nor does the CD spectrum differentiate the two states.[9,10] Adamson's rules correctly predict loss of en (again, one ended and protonated) as the major path of aquation. Similarly, the Vanquickenborne and Ceulemans theory[6] predicts axial en labilization in the $^4E(^4T_2)$ state; the bond energy in that state (Table II) is higher for CN^- ligand by 5900 cm^{-1} than for en. As in the case of the trans, the lower component of the first excited quartet state should lead exclusively to en loss. Experimentally, we find en to be the dominant path but that CN^- is also lost to an appreciable extent (proton uptake represents the sum of protonated one-ended en and protonated cyanide). It seems unlikely that this could be accounted for with the Vanquickenborne and Ceulemans theory via the ^4E state. However, the $^4B_2$ state lies very close in energy to the ^4E, so that it could be populated in a thermal equilibrium between these two states, although its population would be small. But even in that state, en is, according to bond energies, the favored mode of labilization. Results on analogous systems often show considerably less discrimination than would be expected on the basis of Vanquickenborne and Ceulemans theory; the

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(12) Baker, W. A.; Phillips, M. G. *Inorg. Chem.* **1966**, *5*, 1042.

(13) Geis, W.; Schläfer, H. L. *Z. Phys. Chem.* (*Frankfurt am Main*) **1969**, *65*, 107.

discrepancy here is simply too large.

Part of this energy difference could be made up if it was assumed that reaction occurs from the $^4B_2$ state formed directly by absorption prior to internal conversion. If that were the case, one might well expect a wavelength effect. Although we show a small wavelength change of the quantum yields, that change is within experimental error.

It must be pointed out that the substrates are somewhat unstable on ion exchange resins; we could not use HPLC in the analysis, as has been done previously so successfully,[14] because of decomposition. The analysis for free cyanide required brief (30 s) contact with an anion-exchange resin, and this proved satisfactory for the starting materials: *cis*- and *trans*-$Cr(en)_2(CN)_2^+$. As pointed out in the Experimental Section, however, we have evidence for some thermal decomposition of the photochemical product in the solution and on the anion resin. For this reason, the quantum yields for cyanide release, if in error, may be somewhat high.

Acknowledgment. The authors thank the Natural Sciences and Engineering Research Council Canada for financial support.

Registry No. *cis*-$Cr(en)_2(CN)_2^+$, 53302-06-0; *trans*-$Cr(en)_2(CN)_2^+$, 72074-79-4; *cis*-$[Cr(en)_2(CN)_2](ClO_4)$, 56848-41-0; *trans*-$[Cr(en)_2(CN)_2](ClO_4)$, 72074-80-7; *trans*-$[Cr(en)_2Br_2]Br$, 17993-14-5.

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(14) Wong, C. F. C.; Kirk, A. D. *Inorg. Chem.* **1976**, *15*, 1519.

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Intermediates in the Mercury-Photosensitized Reactions of Pentaborane(9)

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Received June 28, 1979

We have investigated the Hg-photosensitized reactions of selectively deuterated pentaboranes including 1-DB_5H_8 and (μ-D)B_5H_8. From the proportions of H_2, HD and D_2 in the photolysis products we conclude that the primary reactive intermediate leading to decaborane(14) and -(16) is pentaborane(7) resulting from direct loss of molecular hydrogen. The elimination of H_2 from any pair of H sites in pentaborane is a random but not strictly statistical process. The existence of the free-radical intermediate B_5H_8 is not substantiated. Supportive mechanistic information is obtained from experiments with 1-methyl- and 2-methylpentaboranes.

Introduction

There is little physical evidence for postulating free-radical intermediates in the mechanisms of boron hydride pyrolyses. However, photochemical studies of B_5H_9 have suggested the presence of an intermediate B_5H_8 radical to account for the formation of $B_{10}H_{16}$ as one of the isolable reaction products.[1] Burwasser and Pease[2] predicted the photochemical formation of B_5H_8 in the 184.9-nm irradiation of pentaborane and deuterium. In the gas-phase radiolysis of pentaborane, Subbanna, Hall, and Koski[3] observed the formation of $(B_5H_8)_2$. They proposed a mechanism in which two B_5H_8 radicals couple to form decaborane(16). Grimes and co-workers[4] suggested using a glow discharge to react the postulated pentaboranyl free-radical reaction intermediate with other molecules. Wang et al.[5] investigated the proton-transfer reaction for a series of bases (R) and obtained information on the stability of B_5H_8.

$$B_5H_9^+ + R \rightarrow B_5H_8 + RH^+ \qquad (1)$$

The photochemical preparation of $B_{10}H_{16}$ reported by Plotkin and Sneddon[1] was suggested to proceed by a free-radical mechanism.

$$Hg(^1S_0) \xrightarrow[253.7\ \text{nm}]{h\nu} Hg(^3P_1) \qquad (2)$$

$$Hg(^3P_1) + B_5H_9 \rightarrow Hg(^1S_0) + B_5H_8 + H \qquad (3)$$

$$2B_5H_8 \rightarrow B_{10}H_{16} \qquad (4)$$

It is difficult to obtain mechanistic information on these complex reactions solely from product analysis without the use of isotopic labels. Out interest in photochemical intermediates has led to a reexamination of the reaction of $Hg(^3P_1)$ with pentaborane. Our experimental approach is to investigate the photochemical behavior of selectively deuterated pentaboranes and examine the isotopic composition of the reaction products. Photosensitization reactions of 1-methyl- and 2-methylpentaboranes are also investigated.

Experimental Section

Instrumentation and Methods. Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer using 3-in. gas cells with either sodium chloride or potassium bromide optics. The cells were thoroughly purged with dry nitrogen after cleaning, and background spectra were run before and after employing the cells. Proton NMR spectra were obtained on either a Varian EM-390 or A-60A spectrometer. ^{11}B NMR spectra were run on a Bruker HX-90 high-resolution spectrometer in the CW mode. Samples were sealed in vacuo with carbon disulfide solvent. Unless otherwise noted, electron-impact mass spectra were obtained on a Consolidated Electrodynamics Corp. Model 21-103A spectrometer at 70-eV ionizing voltage. Other mass spectra were acquired with an AE1-MS902 instrument. Photoionization mass spectra were obtained with the instrument described by DeStefano and Porter,[6] employing lithium fluoride optics and the 121.6-nm α-Lyman emission of hydrogen as the ionizing radiation. Chemical ionization mass spectra in methane were run on the Finnigan Model 3300 gas chromatograph/mass spectrometer employing the gas-inlet system.

Gas chromatograms were obtained on an F and M Corp. Model 810 research gas chromatograph using a flame ionization detector. A 6 ft × $^1/_4$ in. o.d. column operated at 100 °C with 3% OV-101 on 80/100 Chromasorb W-HP support was found to be sufficient for the separation of the decaborane derivatives investigated in this work. Mass spectra (electron impact and chemical ionization) of the decaboranes in carbon disulfide were obtained with the Finnigan Model 3300 gas chromatograph/mass spectrometer with a Systems Industries System 150 data system.

The composition of partially deuterated pentaboranes was resolved from the analysis of the photoionization mass spectra. The absence of fragmentation of the molecular ions produced a spectrum that was a simple summation of the normal isotopic distributions of the parent

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(1) J. S. Plotkin and L. G. Sneddon, *J. Chem. Soc., Chem. Commun.*, 95, (1976).

(2) H. Burwasser and R. N. Pease, *J. Phys. Chem.*, **60**, 1589 (1956).

(3) V. V. Subbanna, L. H. Hall, and W. S. Koski, *J. Am. Chem. Soc.*, **86**, 1304 (1964).

(4) R. Grimes, F. E. Wang, R. Lewin, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U.S.A.*, **47**, 996 (1961).

(5) J. S. Wang, A. DeStefano, and R. F. Porter, *Inorg. Chem.*, **17**, 1374 (1978).

(6) A. DeStefano and R. F. Porter, *Inorg. Chem.*, **14**, 2882 (1975).

0020-1669/80/1319-0447$01.00/0