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The Photochemical Reduction of Octacyanomolybdate(V) in Aqueous Solution[1]

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Received April 16, 1971

The photochemical reduction of octacyanomolybdate(V), $Mo(CN)_8^{3-}$, in aqueous solution by irradiation with light of 365- and 436-nm wavelength has been investigated. In neutral or acidic media $Mo(CN)_8^{3-}$ is efficiently photoreduced to the red heptacyanoaquomolybdate(IV) ion, $Mo(CN)_7H_2O^{3-}$. In basic solution the yellow heptacyanohydroxomolybdate(IV), $Mo(CN)_7OH^{4-}$, is first formed, but this undergoes fast hydrolysis to the blue tetracyanooxohydroxomolybdate(IV) ion, $Mo(CN)_4O(OH)^{3-}$. In all cases cyanogen, C_2N_2, and another nitrogen-containing species formed by oxidation of CN^- are also formed as products and hydrogen ion is released. In contrast to previous reports, no oxygen or hydrogen peroxide could be detected after photolysis. Quantum yields for the reaction are dependent on pH, varying from 1.5 to 4.3 as the pH is varied from 4.0 to 9.0, respectively. Evidence for various dark reactions has been obtained and a reaction mechanism accounting for the high quantum yields has been postulated.

There has been considerable recent interest in the photochemistry of transition metal complexes[2,3] and a number of studies of the photochemical reactions of transition metal cyanides have been reported.[4-6] The photochemistry of octacyanomolybdate(IV), $Mo(CN)_8^{4-}$, has been extensively investigated,[7-9] although the mechanism of its photochemical reactions has not been entirely clarified. Little work, however, has been done on the much more photosensitive octacyanomolybdate(V), $Mo(CN)_8^{3-}$. Early work reported that the ion decomposed readily in light to give HCN, molybdic acid, and $Mo(CN)_8^{4-}$.[10] More recently it has been found that cyanogen, C_2N_2, is formed during photolysis,[11] while a more detailed study suggested oxygen and hydrogen peroxide are the products in addition to $Mo(CN)_8^{4-}$.[12] The work reported here was undertaken in an effort to clarify the conflicting results in the literature and to determine in some detail the mechanism of this interesting and efficient photochemical process.

Experimental Section

Materials.—All compounds were prepared from reagent grade chemicals. $K_4Mo(CN)_8 \cdot 2H_2O$ was prepared by the method of Van de Poel and Neumann[13] and analyzed spectrophotometrically.[14] Solutions of $K_3Mo(CN)_8$ were prepared by the oxidation procedure of Bucknall and Wardlaw[10] and analyzed spectrophotometrically.[14] $Ag_3Mo(CN)_7(H_2O)$ and $H_4Mo(CN)_8 \cdot 5H_2O$ were prepared by the method of Mitra, Sharma, and Mohan.[15] $K_3Mo(CN)_4O(OH) \cdot 2H_2O$ was prepared by irradiating a basic $K_4Mo(CN)_8 \cdot 2H_2O$ solution in bright sunlight until it was a dark blue.[11] Blue crystals were precipitated by the addition of ethanol to the cooled solution. The solid was recrystallized twice from water by the addition of ethanol. The absorption maxima for these complexes are collected in Table I.

TABLE I
ABSORPTION MAXIMA OF MOLYBDENUM CYANIDE COMPLEXES

Complex	λ_{max}, nm	ϵ
$K_4Mo(CN)_8 \cdot 2H_2O$	420 sh	90.3
and $H_4Mo(CN)_8 \cdot 6H_2O$	368	170
	241	15,600
$K_3Mo(CN)_8$	388	1,360
	268	2,610
	255	2,540
$K_3Mo(CN)_7(H_2O)$	512	90
	368	170
$K_3Mo(CN)_4O(OH) \cdot H_2O$	595	35
	235 sh	14,000
	226	18,100
	211	21,500

Water, redistilled from an all-glass system (pH range 5.5–6.5), was used in all solutions. Deuterium oxide, 98.85 mol %, was obtained from Bio-Rad Laboratories, Richmond, Calif.

Photolysis Apparatus.—The light source was a two-electrode P.E.K. 500-W near point-source mercury lamp. The light was collimated by a double convex quartz lens (f = 6 in.) and passed through a 2-cm quartz filter cell containing a 10% w/v $CuSO_4 \cdot 5H_2O$ in 0.01 N H_2SO_4 solution. The desired wavelength was selected by an appropriate Bausch and Lomb interference filter. The 365-nm filter had a half-bandwidth of 20 nm and the 436-nm filter had a half-bandwidth of 12 nm. The light intensity was measured using the ferrioxalate actinometer.[16] The maximum light intensities for both the 365- and 436-nm filter systems were approximately 7×10^{-9} einstein sec^{-1}. The intensity at the sample was varied by passing the light beam through an adjustable diaphragm placed between the $CuSO_4$ and interference filters. Samples were irradiated in 1.000-cm quartz spectrophotometer cells held in a Beckman DU cell holder and stirred with a small magnetic stirring bar. The constant-temperature room where the apparatus was located maintained the temperature at the cell holder at 25 ± 1° during the sample runs.

Analytical Methods.—Ultraviolet–visible spectra were obtained on a Cary 15 recording spectrophotometer. Mass spectra were run on a Hitachi (Perkin-Elmer) RMU-6E mass spectrometer.

Cyanogen was detected qualitatively by the method of Feigl and Hainberger.[17] In addition, the mass spectrum of the gas above the solution after photolysis showed a strong peak at mass 52 which was not present before photolysis. Cyanogen was determined quantitatively by purging the gas into 1 M NaOH

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and analyzing the CN^- ion formed from its disproportionation into CN^- and CNO^- by titration with $AgNO_3$.[17] The other nitrogen-containing product formed by oxidation of cyanide ion was determined by hydrolyzing it to NH_4^+ ion with dilute H_2SO_4, making the solution basic with NaOH, and distilling the NH_3 into standard 0.001 *M* HCl solution.[18] The excess HCl was titrated with NaOH using a pH meter to determine the end point. Hydrogen ion concentrations were calculated from pH measurements assuming that $a_{H^+} = [H^+]$.

The change in the $Mo(CN)_8^{3-}$ ion concentration was followed by the change in the absorbance at 388 nm (ϵ_{388} 1360). The measured absorbances were corrected for the absorption due to the Mo(IV) complexes present, when necessary.

To determine if H_2O_2 was present ferric ion was added to the solution after photolysis and the $N_2:O_2$ peak ratio in the mass spectrum of the gas above the solution was measured. To check the sensitivity of the method, two deaerated solutions of 4.50×10^{-3} *M* $K_3Mo(CN)_8$ were photolyzed for 20 min (essentially complete reduction). After photolysis, 10^{-4} *M* H_2O_2 was added to one solution and the gas samples above both solutions were analyzed in the mass spectrometer. The sample containing the added H_2O_2 showed a $N_2:O_2$ peak ratio of 1.4 ± 0.3, while the other sample gave the same ratio as a deaerated unphotolyzed solution, 3.5 ± 0.5. Since the reproducibility of the $N_2:O_2$ peak ratio is about ±25%, the method will easily detect 5×10^{-5} *M* O_2. Additionally, the photolyzed solutions were qualitatively tested for H_2O_2 by the addition of luminol (3-aminophthalhydrazide) and $K_3Fe(CN)_6$, which produce a brilliant blue-white chemiluminescence in the presence of H_2O_2.[19] No chemiluminescence was observed for the photolyzed solutions, while that with the added 10^{-4} *M* H_2O_2 gave a positive test.

Attempts to detect O_2 formed in the photolysis were made by three methods. First, a Gilson Medical Electronics Oxygraph with a Clark oxygen electrode was used to measure directly the O_2 in solution after complete photolysis of a 4.50×10^{-3} *M* deaerated sample of $K_3Mo(CN)_8$. The sensitivity and reproducibility of the instrument were found to be $(2.5 \pm 0.5) \times 10^{-5}$ *M* O_2. In no case was O_2 above this level detected in the photolyzed solutions. Second, 4.50×10^{-2} *M* deaerated solutions were purged with He gas after complete photolysis into standard chromous solutions and the increase in chromic ion was measured spectrophotometrically. The maximum change in absorption corresponded to $(1.0 \pm 0.2) \times 10^{-6}$ *M* O_2, the same value obtained from unphotolyzed solutions. Solutions containing $\sim 10^{-4}$ *M* O_2 used as standards gave good results and the method is sensitive to $\sim 10^{-5}$ *M* O_2. Third, the gas above the solution after photolysis was analyzed with the mass spectrometer as described in the H_2O_2 analysis, and no decrease in the $N_2:O_2$ ratio was observed.

Quantum Yields.—Product quantum yields (Φ) were determined by following the disappearance of $Mo(CN)_8^{3-}$. Corrections for the absorption of product were made where necessary. Since most of the quantum yields were determined for the first 10% reduction only, these corrections were generally negligible. Also, in cases of very low concentration ($\sim 10^{-4}$ *M*), a correction was necessary for light intensity since not all the incident light was absorbed. This correction was made using Beer's law and the known molar absorptivities.

Results and Discussion

Qualitive Observations.—When aqueous solutions of $Mo(CN)_8^{3-}$ were exposed to irradiation at 365 or 436 nm in neutral or acidic solution, they rapidly lost their yellow color, becoming first red and then, with longer irradiation times, blue. In basic solution, the color change was first to darker yellow, then green, and finally blue, and the color changes were considerably more rapid than at neutral (pH ~6.0) or acidic pH. The decrease in absorbance of $Mo(CN)_8^{3-}$ with photolysis time is plotted in Figure 1.

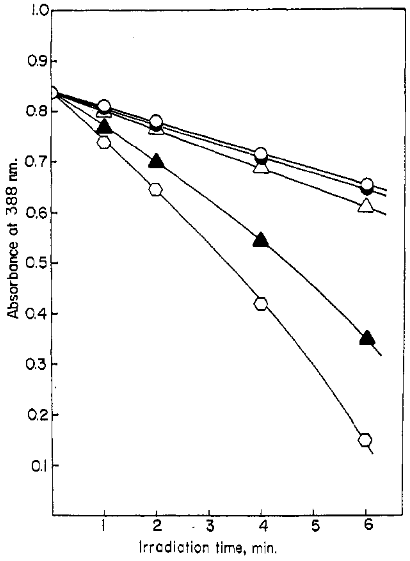

Figure 1.—Absorbance at 388 nm as a function of irradiation time of $Mo(CN)_8^{3-}$ under various pH conditions; $[Mo(CN)_8^{3-}]_0 = 6.17 \times 10^{-3}$ *M*, λ irradiation 365 nm: ○, D_2O, neutral, unbuffered; ●, H_2O, neutral, unbuffered; △, pH 4.00; ▲, pH 7.00; ○, pH 9.00.

Several authors have reported similar changes in color when solutions of $Mo(CN)_8^{4-}$ are irradiated.[7-9] There has been considerable disagreement in the literature concerning the nature of the red intermediate.[2,3,20] Adamson and Perumareddi[2,3,9] have formulated it as $Mo(CN)_7H_2O^{3-}$, formed by the photochemical replacement of CN^- by H_2O. Jacob and coworkers, on the other hand,[2,3,8] have proposed it to be $Mo(CN)_8(H_2O)_2^{4-}$, a decacoordinated species. The recent isolation of the silver salt of the red intermediate and the determination of its properties[15] have provided strong evidence in support of the $Mo(CN)_7H_2O^{3-}$ structure. Although the red intermediate has been reported as occurring in the photolysis of $Mo(CN)_8^{4-}$ in basic solution at very high light intensities,[9] it is not observed ordinarily and the major initial photoproduct under basic conditions appears to be the yellow $Mo(CN)_7OH^{4-}$.[15] Evidence for this ion as a major product in base was obtained by the demonstration that it is obtained from the red intermediate by titration with base[15]

$$Mo(CN)_7H_2O^{3-} + OH^- \longrightarrow Mo(CN)_7OH^{4-} + H_2O$$

The yellow $Mo(CN)_7OH^{4-}$ is then rapidly converted in base to the well-characterized[2] blue $Mo(CN)_4O(OH)^{3-}$ either by further photolysis or by basic hydrolysis

$$2OH^- + Mo(CN)_7OH^{4-} \longrightarrow Mo(CN)_4O(OH)^{3-} + H_2O + 3CN^-$$

In order to determine if the same red species is formed from $Mo(CN)_8^{3-}$ upon photolysis in neutral or acidic solution, the changes in the absorption spectrum with irradiation of both $Mo(CN)_8^{4-}$ and $Mo(CN)_8^{3-}$ were compared (Figure 2). The red intermediate obtained in the photolysis of $Mo(CN)_8^{4-}$ has an absorption maximum at 512 nm, accounting for its color.[15] As can be seen, the absorption at 512 nm increased rapidly at first for both complexes and the spectra for both became almost identical when the 512-nm absorption was maximum. After a longer irradiation time this red color disappeared and the spectrum became that

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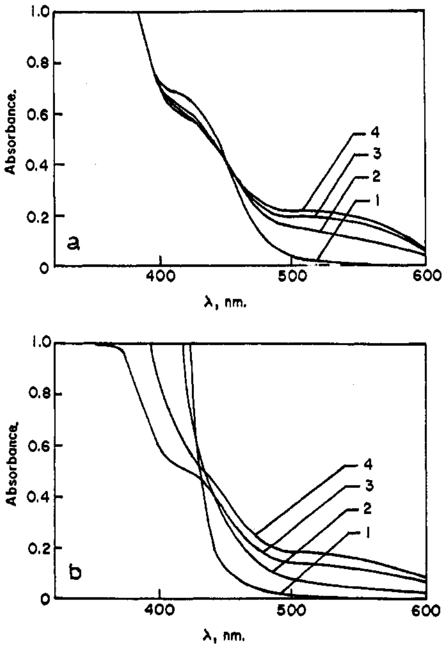

Figure 2.—Absorption spectra of $Mo(CN)_8^{4-}$ and $Mo(CN)_8^{3-}$ solutions irradiated for various times at 365 nm, 7.10 × 10^{-3} *M*: (a) $Mo(CN)_8^{4-}$: 1, 0 min; 2, 10 min; 3, 20 min; 4, 40 min; (b) $Mo(CN)_8^{3-}$: 1, 0 min; 2, 30 min; 3, 45 min; 4, 60 min.

of the final blue product, $Mo(CN)_4O(OH)^{3-}$. It seems reasonably certain, then, that the initial product in the photolysis of $Mo(CN)_8^{3-}$ is the red $Mo(CN)_7H_2O^{3-}$, the same species that appears to be first formed in the photolysis of $Mo(CN)_8^{4-}$.[9,15] In basic solution, this hydrolyzes immediately to yellow $Mo(CN)_7OH^{4-}$.

Product Analysis.—Qualitative analysis of the photolyzed solutions indicated that in addition to $Mo(CN)_7H_2O^{3-}$, cyanogen (in agreement with Perumareddi)[14] and another nitrogen-containing oxidation product of CN^- (Q) are produced. The ratios of C_2N_2 and Q to $Mo(CN)_8^{3-}$ reduced are found in Table II. The large uncertainty in the values at high pH are due to the disproportionation of C_2N_2 into CN^- and CNO^- [17] during the time required to make the analyses. All attempts to detect the presence of oxygen or hydrogen peroxide as photolysis products gave negative results. In neutral, unbuffered solution it was found that photolysis caused a rapid drop in pH, corresponding in time to the disappearance of the reactant. Moreover, it was observed that this drop in pH occurred only during photolysis, since interruption of the light beam resulted in the pH remaining constant until irradiation was begun again. By measuring the change in pH and comparing it with the change in absorbance of the reactant a value of 0.30 ± 0.02 H^+ released for each $Mo(CN)_8^{3-}$ reduced was obtained.

TABLE II

RATIOS OF C_2N_2 AND Q PRODUCED TO $Mo(CN)_8^{3-}$ REDUCED AT 365-NM IRRADIATION

Soln	$C_2N_2:Mo(CN)_8^{3-}$	$Q:Mo(CN)_8^{3-}$
Unbuffered, H_2O[a]	0.25 ± 0.02	0.30 ± 0.02
pH 4.0 buffer[a]	0.24 ± 0.06	0.24 ± 0.05
pH 9.0 buffer[b]	0.15–0.30	0.20–0.30

[a] Average of four or more determinations. [b] Range of five or more determinations.

TABLE III

PRODUCT QUANTUM YIELDS, Φ, FOR PHOTOREDUCTION OF $Mo(CN)_8^{3-}$ UNDER VARIOUS CONDITIONS

Soln	λ irradn, nm	$[Mo(CN)_8^{3-}]_0$, 10^3 *M*	I_0, 10^9 einsteins sec^{-1}	Irradn time, min	Φ
Neutral, nonbuffered, H_2O	365	4.50–5.40	6.30–7.50	1–10	1.59 ± 0.06[a]
		6.36	3.28	45	1.52
		6.36	0.0917	120	1.41
		6.10	7.61	3	1.56
		2.42	7.61	3	1.64
		0.612	7.61	0.5	1.67
	436	6.31	7.72	10	1.64
Neutral, nonbuffered, D_2O	365	4.20–6.20	6.60	1–10	1.46 ± 0.05[a]
pH 4.0 buffer	365	4.50–5.40	6.30–7.50	1–5	1.51 ± 0.08[a]
		5.94	4.61	2.6	1.50
		5.94	3.14	2.6	1.56
		5.97	0.527	90	1.57
		6.39	0.0852	480	1.41
	436	5.60	7.72	10	1.61
pH 7.0 buffer	365	3.70–5.70	7.60	1–4	3.10 ± 0.10[a]
pH 9.0 buffer	365	4.50–5.40	6.30–7.50	1–6	4.29 ± 0.50[a]
		13.2	6.67	1	4.41
		6.30	6.67	1	4.36
		2.20	6.67	1	4.59
		6.31	6.67	3	4.59
		6.31	0.757	15	4.71
		6.31	0.0942	60	5.31
	436	5.49	7.72	4	4.20

[a] Ten or more runs. All others are averages of duplicates.

Quantum Yields.—The product quantum yields (Φ) under a variety of conditions are found in Table III. As can be seen, the product quantum yield was found to be greater than 1 in all cases, varying from 1.5 at pH 4.00 to 4.3 at pH 9.00. As with the product analyses, the larger uncertainty in Φ at high pH is due to cyanogen disproportionation[17] during the time required for determination of Φ. Variation in initial concentration of reactant, light intensity, or wavelength had little influence on the quantum yields, while only a slight isotope effect was found in D_2O. These product quantum yields are on the average about 25% lower than those previously reported for comparable conditions.[12] The reason for this difference is not apparent.

Dark Reactions.—Because of the large quantum yields and the nature and distribution of products it is clear that one or more secondary dark reactions are occurring after the initial photochemical process. The simple photochemical reaction suggested by Adamson, *et al.*, accounts only for the production of the red species and cyanogen and would give a maximum product quantum yield of 1[2]

$$H_2O + Mo(CN)_8^{3-} \xrightarrow{h\nu} Mo(CN)_7H_2O^{3-} + {}^1/_2C_2N_2$$

It was observed that the addition of cyanide ion in the dark to a solution of $Mo(CN)_8^{3-}$ at pH 9.00 resulted in an essentially instantaneous reduction of an equivalent amount of $Mo(CN)_8^{3-}$ to $Mo(CN)_8^{4-}$. This rapid reduction was followed by a much slower reduction of a second equivalent of $Mo(CN)_8^{3-}$, with the overall stoichiometry eventually reaching 2 mol of $Mo(CN)_8^{3-}$ per mol of CN^-. As the pH was lowered, the reaction with CN^- became slower until at pH 4.00 no detectable reduction occurred. Clearly, the reactive species in this dark reaction is CN^- which is present in extremely small quantities in acidic solution (pK_a(of HCN) = 9.4).

Cyanogen disproportionates in base, giving equal amounts of CN^- and CNO^-.[17] At pH 9.00, this rate was found to be measurable but not fast enough to occur to a great extent during the time of photolysis. This disproportionation, however, accounts for the slow reduction of the second equivalent of $Mo(CN)_8{}^{3-}$ observed in the dark reaction with CN^-

$$2Mo(CN)_8{}^{3-} + 2CN^- \longrightarrow 2Mo(CN)_8{}^{4-} + C_2N_2 \quad \text{(fast)}$$

$$2OH^- + C_2N_2 \longrightarrow CN^- + OCN^- + H_2O \quad \text{(slow)}$$

These reactions do not occur in acidic solution and go only to a limited extent at neutral pH.

Since the final reduction product obtained in basic solution is $Mo(CN)_4O(OH)^{3-}$, it seemed possible that hydrolysis of the initial photoreduction product in basic solution, $Mo(CN)_7OH^{4-}$, might occur in the dark, releasing additional cyanide ion. In order to test this, solutions of the red $Mo(CN)_7H_2O^{3-}$, obtained from $Ag_3Mo(CN)_7(H_2O)$,[15] were prepared at pH 4.00, neutral pH, and pH 9.00 in the dark and their stabilities determined by observing the change of the absorbance at 512 nm with time. Over a 10-min period the absorbance at 388 nm of the acid solution did not change, that of the neutral solution decreased slightly, and that of the basic solution had decreased greatly, and the spectrum had essentially changed to that of $Mo(CN)_4O(OH)^{3-}$. Additionally, a solution of $Mo(CN)_8{}^{3-}$ at pH 4.00 was irradiated until the red species was maximum and the product quantum yield was determined, giving a value for Φ of 1.59. The solution was then quickly adjusted to pH 9.00 with KOH and the quantum yield again measured after 10 min in the dark, giving a new value for Φ of 4.13. Under the same conditions, a solution of $Mo(CN)_8{}^{3-}$ in the dark showed no change from the original spectrum. Clearly, the hydrolysis of the initial photoreduction product in base is a fast dark reaction, releasing additional CN^- into the solution

$$2OH^- + Mo(CN)_7OH^{4-} \longrightarrow Mo(CN)_4O(OH)^{3-} + 3CN^- + H_2O$$

This additional CN^- can then reduce more $Mo(CN)_8{}^{3-}$ as described above, thus accounting for the high quantum yields in base. In acid this dark hydrolysis reaction does not occur and any CN^- released by the photochemical hydrolysis of the red $Mo(CN)_7H_2O^{3-}$ to give the blue $Mo(CN)_4O(OH)^{3-}$ is tied up as HCN. At pH between 4.00 and 9.00 the hydrolysis reaction obviously proceeds at a rate dependent on the pH.

Kinetics.—As seen in Figure 1, the reaction is zero order. The small departure from zero-order kinetics at long reaction times in basic solution is most likely due to the slow disproportionation of C_2N_2. Consideration of Figure 1 indicates a 10–20% contribution from this source at pH 9.00 after 6 min of irradiation.

Mechanism.—In order to provide a reasonable understanding of the photochemical reduction of $Mo(CN)_8{}^{3-}$, a mechanism must explain satisfactorily (1) the formation and distribution of the products; (2) the product quantum yields in both acidic and basic solution; (3) the lack of effect on the quantum yield with variation of initial reactant concentration and light intensity; and (4) the observed kinetics.

Ligand field considerations indicate the single electron of $Mo(CN)_8{}^{3-}$ resides in the $d_{x^2-y^2}$ orbital in the ground state.[14] Absorption of light excites this electron to a higher energy d orbital, and the lack of wavelength effect suggests the reactive excited state is the same lowest excited state for both wavelengths. Since both wavelengths are close to the same absorption band (388 nm), however, the same initial excited state may be involved.

The dark reduction of $Mo(CN)_8{}^{3-}$ by released CN^- could give product quantum yields up to 4 in basic solution. In order to explain the quantum yields in acidic solution and the somewhat greater than 4 quantum yields in basic solution another dark reaction must be postulated. The general photolytic mechanism of Adamson and Sporer[4] has been applied here, leading to the following proposed reactions in acidic solution

$$Mo(CN)_8{}^{3-} \xrightarrow{h\nu} Mo(CN)_7 \cdot CN^{3-} \tag{1}$$

$$H_2O + Mo(CN)_7 \cdot CN^{3-} \xrightarrow{k_2} Mo(CN)_7H_2O \cdot CN^{3-} \tag{2}$$

$$Mo(CN)_7H_2O \cdot CN^{3-} \xrightarrow{k_3} Mo(CN)_7H_2O^{3-} + CN\cdot \tag{3}$$

$$H_2O + Mo(CN)_7H_2O \cdot CN^{3-} \xrightarrow{k_4} Mo(CN)_7H_2O^{3-} + P \tag{4}$$

$$Mo(CN)_8{}^{3-} + P \xrightarrow{k_5} Mo(CN)_8{}^{4-} + Q \tag{5}$$

$$2CN\cdot \longrightarrow C_2N_2 \tag{6}$$

In this mechanism reaction 1 is a light-induced homolytic fission of one cyanide ligand leading to the radical pair. Reaction 2 is the interposition of a solvent water molecule, while reactions 3 and 4 indicate two routes for reaction of this hydrated species: homolytic cleavage of the radical pair, giving $CN\cdot$, and the formation of a reactive intermediate, P, by further hydrolysis of the radical pair. P has been suggested by Adamson, from a study of the reduction of $Fe(CN)_6{}^{3-}$, to be $O{=}\dot{C}NH_2$.[21] The subsequent fast reduction of a second $Mo(CN)_8{}^{3-}$ by P (reaction 5) accounts for the product quantum yield being greater than 1, while the relative rates of reactions 3 and 4 determine the exact value of Φ. The product, Q, which upon acid hydrolysis produces $NH_4{}^+$, could be HCNO (or CNO^- depending on pH), the most likely species obtainable by a two-electron oxidation of CN^-. If Q is HCNO, this would explain the drop in pH upon photolysis in unbuffered solution with the formation of about 0.30 H^+ for each $Mo(CN)_8{}^{3-}$ reduced, since the overall oxidation of CN^- to HCNO produces 1 H^+ for each HCNO.

In basic solution the same reactions occur and, in addition, the fast hydrolysis and reduction reactions discussed above

$$Mo(CN)_7H_2O^{3-} + OH^- \longrightarrow Mo(CN)_7OH^{4-} + H_2O \tag{7}$$

$$Mo(CN)_7OH^{4-} + 2OH^- \longrightarrow Mo(CN)_4O(OH)^{3-} + 3CN^- + H_2O \tag{8}$$

$$Mo(CN)_8{}^{3-} + CN^- \longrightarrow Mo(CN)_8{}^{4-} + CN\cdot \tag{9}$$

From a steady-state treatment of the reaction intermediates, the rate expressions for the reduction of the $Mo(CN)_8{}^{3-}$ ion in acidic and basic solutions are, respectively

$$\text{rate} = -d[Mo(CN)_8{}^{3-}]/dt = \phi I_a \left[\frac{k_3 + 2k_4}{k_3 + k_4}\right]$$

$$\text{rate} = -d[Mo(CN)_8{}^{3-}]/dt = \phi I_a \left[\frac{4k_3 + 5k_4}{k_3 + k_4}\right]$$

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where ϕ is the primary quantum yield for reaction 1 and I_a is the absorbed light intensity. If it is assumed that all the incident light is absorbed, which is a good approximation for the first 10–20% reaction where the product quantum yields were generally measured, it is seen that the rates and thus Φ (product quantum yield) are independent of initial concentration of $Mo(CN)_8^{3-}$ and that the expression leads to zero-order kinetics, in agreement with the experimental results. Furthermore, consideration of the expressions indicates Φ must also be independent of light intensity, also in agreement with the results. The rate expressions indicate the product quantum yield in acidic solution must lie between 1 and 2 and in basic solution between 4 and 5, depending on the values of k_4 and k_3, again in agreement with the results. Finally, if the mechanism is valid, the primary quantum yield, ϕ, using the observed values for Φ of 1.5 and 4.3 and assuming $k_4 \gg k_3$, must have a minimum value of 0.75 in acidic solution and 0.86 in basic solution. Using the observed product distribution (Table II) a ratio of k_3/k_4 can be calculated, which leads to a calculated value of ϕ of 1.1 ± 0.4, suggesting a primary quantum yield of unity.

Acknowledgment.—This work was supported by U. S. Public Health Service Grant GM 08347, National Institute of General Medical Sciences, and by Research Career Development Award 5-K3-GM 22,643, to J. T. S. Special thanks are due to Dr. W. M. Moore of this department for the use of much of the photochemical apparatus, purchased in part by funds from U. S. Public Health Service Grant GM 11401, National Institute of General Medical Sciences.

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The Blue Ruthenium Chloride Complexes and Their Oxidation Products[1]

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Received February 22, 1971

Three blue ruthenium chloride complexes have been identified as dimeric ruthenium(II,III) species of the type $Ru_2Cl_{3+n}^{(2-n)+}$, where $n = 0, 1, 2$. Chemical and controlled-potential oxidations produce corresponding dimeric ruthenium(III) complexes. The oxidation state of the metal was verified by redox titration and magnetic measurements. Ionic charges were measured by ion-exchange membrane equilibrations. The electrochemical behavior of these complexes is also reported.

The blue ruthenium chloride complexes were first observed by Claus,[2] who noted that when ruthenium trichloride was heated with strong reducing agents, intense blue solutions were obtained. Other investigators postulated on rather limited data that these blue solutions contained ruthenium(II) chloride complexes. The most recent reports on these complexes have been made by Adamson[3] and Wilkinson.[4] Although Adamson was able to elute a discrete band from an anion column with 4.0 *M* HCl, no attempt was made to characterize this species. The magnetic moment of this solution was determined in 10–11 *M* HCl and found to be on the order of 2.12–2.35 BM, which is inconsistent with both high-spin and low-spin ruthenium(II) complexes. He suggested an equilibrium between high- and low-spin complexes could account for the observed magnetic moment. Wilkinson[4] prepared blue ruthenium chloride solutions and was able to precipitate a dinegative ruthenium-containing ion, which he identified as $Ru_5Cl_{12}^{2-}$. He noted that these compounds were weakly paramagnetic and showed a single resonance in the esr spectrum.

Experimental Section

Analysis.—Ruthenium was determined spectrophotometrically as RuO_4[5] or RuO_4^{2-},[6] depending on whether the analysis was conducted in the presence or absence of free chloride.

Chloride coordinated to ruthenium was determined gravimetrically using a modification of the method reported by Connick and Fine.[7] Excess silver nitrate was added to an aliquot of the sample, and the ruthenium present was oxidized to ruthenium tetraoxide with ceric perchlorate. The RuO_4 was removed by heating. The solution was then filtered and the AgCl was thoroughly washed with 0.01 *M* HNO_3. This precipitate was dissolved in concentrated ammonia and reprecipitated by adjusting the pH to below 7 with nitric acid. This solution was filtered into preweighed crucibles and dried at 110°.

Lanthanum solutions were prepared by dissolving lanthanum oxide (American Potash and Chemical Corp.) in the appropriate acid. Lanthanum was determined gravimetrically by ignition of the oxalate.

Reagents.—Ruthenium chloride (≃38% Ru) was obtained from Engelhard Industries. This was converted into $K_2RuCl_5(H_2O)$ as previously reported.[8] This compound was used as the starting material in the preparation of all the blue complexes.

Ion-exchange resins used were Dowex 50-X8, 200–400 mesh (H^+ form), and Dowex 1-X8, 100–200 mesh (Cl^- form). The cation resin was always washed with 6 *M* HCl to remove iron impurities. The cation-exchange membranes were obtained from American Machine and Foundry Co. (Serial No. C 103 FE).

All other chemicals were reagent grade and were used without further purification.

Equipment.—All ultraviolet–visible spectra were recorded on a Cary Model 14 spectrophotometer using quartz cells. A Beckman Research pH meter was used for pH measurements and for

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[1] Work carried out by P. E. Dumas in partial fulfillment of the Ph.D. degree, University of South Carolina, 1971.

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