

CONTRIBUTION FROM THE ISTITUTO CHIMICO "G. CIAMICIAN" DELL'UNIVERSITÀ, LABORATORIO DI FOTOCHIMICA E RADIAZIONI D'ALTA ENERGIA DEL CNR, BOLOGNA, ITALY, AND ISTITUTO CHIMICO DELL'UNIVERSITÀ, CENTRO NAZIONALE DI CHIMICA DEI COMPOSTI DI COORDINAZIONE ED ELEMENTO-ORGANICI DEL CNR, FERRARA, ITALY

Definite Evidence of a Primary Photoaquation Reaction of the Octacyanomolybdate(IV) Complex Anion

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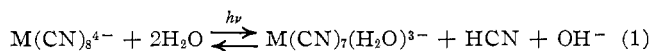
The photochemical behavior of $\text{Mo}(\text{CN})_8^{4-}$ was studied in aqueous and buffered solutions using 365-m μ radiations. Spectrophotometric and pH measurements were used to establish the nature and the kinetics of the photoreaction. Definite evidence was obtained in favor of a primary photoaquation reaction, whose quantum yield was 0.8, independent of the complex concentration and the light intensity. A previously suggested mechanism, based on a primary photoreaction leading to the "supercomplex" $\text{Mo}(\text{CN})_8(\text{H}_2\text{O})_2^{4-}$, is criticized.

Although the photochemistry of the $\text{M}(\text{CN})_8^{4-}$ ions ($\text{M} = \text{Mo}$ or W) has received a good deal of attention,¹⁻¹⁰ neither the mechanism of the photoreactions nor the nature of the products has been fully clarified.

When aqueous solutions of the complexes are irradiated with radiations of wavelength greater than 300 m μ (d-d bands), a red intermediate species is formed at first, and a blue product is then obtained with a more prolonged irradiation.¹¹ The blue final product, which was for a long time thought to be an eight-coordinated species,^{8d,9e} has been recently established as $\text{M}(\text{CN})_4(\text{O})(\text{OH})^{3-}$.¹⁰ However, this result does not help in clearing up the other controversial points, *i.e.*, the nature of the primary photoreaction and the composition of the red intermediate. In fact, there are completely different opinions regarding these two subjects.

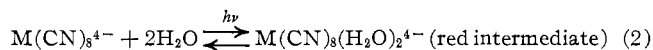
According to Carassiti and coworkers⁹ and to Adam-

son and Perumareddi,^{8b-d} irradiation in the d-d bands causes a simple photoaquation reaction

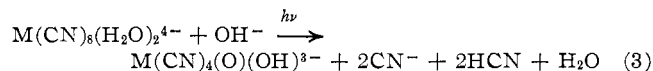


The heptacyano complex is considered to be the red intermediate. Photoreaction 1 is followed by thermal reactions (very rapid in alkaline medium^{9d}) which cause release of other CN^- ions up to a maximum of four (blue final product).

According to Jakob and coworkers,⁷ the primary photoreaction causes the formation of "supercomplexes" as



A secondary *photochemical* reaction should then convert the red intermediate to the blue final product



Some evidence in favor of reaction 1 has been recently criticized.^{7b} In this paper, we report experiments on $\text{Mo}(\text{CN})_8^{4-}$ which strongly support reaction 1 and which cannot be explained on the basis of Jakob's mechanism.

Experimental Section

Materials.— $\text{K}_4[\text{Mo}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ was prepared following the method described in ref 12. All of the other chemicals used were of reagent grade.

Apparatus.—Radiations of 365 m μ were obtained from a Hanau Q 400 mercury-vapor lamp by means of a Schott and Genossin interference double filter ($T_{\text{max}} = 40\%$, half-width = 10 m μ). The reaction cell was a standard spectrophotometric cell (thickness, 1 cm; capacity, 3 ml), housed in a thermostated cell holder. All of the experiments were carried out at 20°. The homogeneity of the solutions was maintained during irradiation by bubbling with a stream of purified N_2 . The incident light was measured by means of a ferric oxalate actinometer,¹³ and the light absorbed was calculated on the basis of the transmittance of the solutions. Different intensity values of the incident light were obtained by placing uniform-density filters in the optical path. Spectrophotometric measurements were performed with an Optica CF4 NI spectrophotometer, and pH measurements were done with a Knick KpH 350 pH meter.

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 (11) Recently, photoelectron production has been found to occur by exciting in the region around 250 m μ (charge-transfer bands).^{8f}

Procedure.—A weighed amount of the complex was dissolved in the selected medium (pure water or buffered solutions) in red light. The concentration of the complex was in the range 5×10^{-2} – 5×10^{-4} *M*. Two cells were filled with 3 ml of freshly prepared solution. One of the cells was placed in the thermostated cell holder of the irradiation equipment. The other cell was placed in a thermostated cell holder maintained in the dark at the same temperature, in order to provide a control for possible thermal reactions (which, however, did not occur). Measurements of pH were accomplished directly in the reaction cell during irradiation by means of a glass-reference combined microelectrode. Spectrophotometric measurements were performed, after suitable irradiation periods, by interrupting the light beam and bringing the reaction cell to the spectrophotometer. The buffer solutions used were 2×10^{-3} , 10^{-3} , or 5×10^{-4} *M* in Na_2HPO_4 and KH_2PO_4 . The ionic strength was always adjusted to 1 by adding Na_2SO_4 . The buffer solutions had a natural pH of ~ 6.5 , and they proved to give, as expected, linear variations of pH *vs.* the concentration of added acid or base within a minimum range of ± 0.5 from their natural pH. As we had to measure the rate of formation of basic species (see below), the buffer solutions used as solvents were brought to pH ~ 6 with dilute HCl in order to make complete use of the range of linear pH variation. The pH of the buffer solutions that contained 0.1 *M* KCN was also adjusted to ~ 6 by adding HCl.

Results

When the experiments were carried out in pure aqueous solution (whose natural pH was ~ 6), an extremely rapid increase in the pH was observed as soon as the irradiation began, regardless of the complex concentration. For example, in the case of a 2×10^{-3} *M* solution, the "dark" pH value was 5.74; 10 and 30 sec of irradiation (absorbed light intensity 2.7×10^{-7} $Nh\nu/\text{min}$) increased the pH value to 7.0 and 8.6, respectively. Continuing the irradiation, the pH still increased but at a diminishing rate, and, for prolonged irradiation, it began to decrease. The maximum pH value was reached within 10–15 min for dilute solutions and after much longer irradiation periods for concentrated solutions.

Reliable data concerning the initial rate of formation of the OH^- ions could not be obtained for pure aqueous solutions, because the pH variations were too rapid in comparison with the time needed for the glass electrode to give its response. Experiments were then carried out in appropriate, slightly buffered media. Such a method, in fact, had previously proved to be a very advantageous one when the rates of formation of acids or bases had to be measured.^{14,15} In the buffered media, a linear increase of the pH *vs.* the light absorbed was obtained (see, for example, Figure 1). By using a calibration plot of the pH of the buffer solutions *vs.* the amount of base added (see Procedure), it was possible to calculate the equivalents of base produced during the irradiation. The ratio of the moles of base produced to the moles of photons absorbed (*i.e.*, the quantum yield of OH^- formation) was independent of the light intensity and complex concentration (Table I).^{16,17} The increase in the pH observed during the first period of irradiation proved to be due to a photoreaction which could be completely reversed in the dark. In fact, irradiating a 5×10^{-2} *M* solution in a buffered

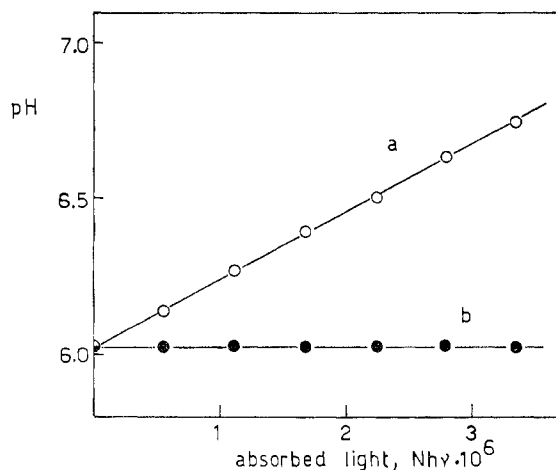


Figure 1.—Plots of the pH *vs.* the absorbed light for 5×10^{-2} *M* $\text{Mo}(\text{CN})_6^{4-}$ buffered solutions containing (a) 0 and (b) 0.1 *M* KCN.

TABLE I
QUANTUM YIELD VALUES FOR THE OH^- PRODUCTION
IN THE PHOTOLYSIS OF $\text{Mo}(\text{CN})_6^{4-}$ AT $365 \text{ m}\mu^a$

[Complex], <i>M</i>	Absorbed light intens, $Nh\nu/\text{min}$	Quantum yield
5×10^{-2}	0.66×10^{-6}	0.82 ± 0.05
5×10^{-2}	0.56×10^{-6}	0.80 ± 0.05
2×10^{-3}	0.33×10^{-6}	0.83 ± 0.05
1×10^{-3}	0.24×10^{-6}	0.83 ± 0.05
5×10^{-4}	0.96×10^{-6}	0.88 ± 0.05

^a Temperature 20° , pH 6–7, ionic strength 1.

medium for 100 sec caused the pH to change from 5.99 to 6.28 (1.68×10^{-4} mol of OH^- produced). When the solution was placed in the dark, the pH decreased to 6.00 in 2 days (1.63×10^{-4} mol of OH^- consumed).

It was also verified that the pH increase during irradiation was accompanied by a noticeable increase in absorbance in the region around $500 \text{ m}\mu$,¹⁸ at the same time, the red color appeared which had been previously noted by all of the authors.

When the irradiation was carried out on buffered solutions containing 0.1 *M* KCN, neither the spectrum nor the pH (Figure 1) changed.

Discussion

The results obtained clearly show that when solutions of $\text{Mo}(\text{CN})_6^{4-}$ are irradiated with $365\text{-m}\mu$ radiations, a primary photoreaction occurs which produces OH^- ions. This conclusion is based on (1) the immediate pH increase upon irradiation, (2) the zero-

(16) The results obtained are in qualitative agreement with those previously reported by Carassiti and Balzani.¹⁶ In that paper, however, the quantum yield of OH^- formation was inferred from the pH variations shown by pure aqueous solutions of the complex. For the reasons explained above, such a method could not give reliable results. In fact, the quantum yield values obtained by measuring pH variations of buffered solutions (Table I) are noticeably higher than those previously reported. In order to confirm the reliability of the quantum yield values obtained in the present work, the method based on the measuring of pH variations in buffered media was used to study the photoaquation of $\text{Co}(\text{CN})_6^{4-}$. A quantum yield of 0.33 was obtained (at $365 \text{ m}\mu$), which agrees well with the value 0.31 previously calculated from spectrophotometric measurements.¹⁷

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(18) The changes in absorbance observed were similar to those reported in Figure 2 of ref 8d.

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order law obtained for the initial formation of OH^- ions, and (3) the constancy of the quantum yield of OH^- production when the concentration of the complex and the light intensity were varied over a wide range.

If the production of OH^- were due to a secondary photochemical reaction, none of the above results could be explained. Thus, the results obtained are in agreement with the mechanism proposed by Carassiti and coworkers and by Adamson and Perumareddi (reaction 1), but they cannot be explained on the basis of Jakob's mechanism.

Our experiments also show that the production of OH^- and the appearance of the red color (*i.e.*, the formation of the red intermediate) are parallel phenomena and are both inhibited by the presence of an excess of KCN. These results can also be explained on the basis of eq 1, but they cannot be accounted for by Jakob's mechanism.

Jakob's mechanism can be criticized for these other reasons.

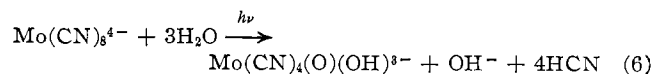
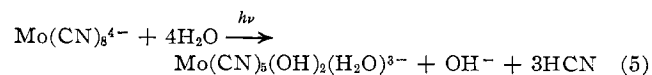
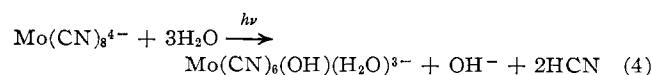
(1) According to Jakob, *et al.*,^{7b} light excitation would change the structure of the anion from a dodecahedral to an antiprismatic one. The latter structure would have two favorable positions, at the centers of its square faces, for the coordination of two H_2O molecules as "outer ligands." These two additional ligands should stabilize the antiprismatic structure and, thus, should not allow a return to the dodecahedron. This mechanism is certainly an attractive one. However, it should be noted that recent studies¹⁹⁻²² have shown that *in solution* the ground-state complex already possesses the antiprismatic structure.

(2) The main evidence in favor of the formation of "supercomplexes" (photoreaction 2) was given by the increase in resistance of $\text{M}(\text{CN})_8^{4-}$ solutions during the irradiation.^{7g,h} This phenomenon has been attributed to "the naturally expected lower mobility of the red $\text{M}(\text{CN})_8(\text{H}_2\text{O})_2^{4-}$ ions than that of $\text{M}(\text{CN})_8^{4-}$."^{7h} It should be noted, however, that the equivalent conductances of $\text{W}(\text{CN})_8^{3-}$ and $\text{Fe}(\text{CN})_6^{3-}$ are practically equal²³ and so are the ionic mobilities of $\text{Mo}(\text{CN})_8^{4-}$, $\text{W}(\text{CN})_8^{4-}$, and $\text{Fe}(\text{CN})_6^{4-}$.²⁴ Therefore, it seems that differences both in size and in geometry do not have a great influence on the conductance of complexes of this type. Accordingly, the presence of two water molecules bonded in an outer sphere should not cause any significant decrease in the mobility of the $\text{M}(\text{CN})_8^{4-}$

anions.²⁵ From Jakob's experiments (Figure 6 of ref 7g) it would appear, on the contrary, that the conductance of the "supercomplex" $\text{Mo}(\text{CN})_8(\text{H}_2\text{O})_2^{4-}$ should be at least 10% lower than that of $\text{Mo}(\text{CN})_8^{4-}$.²⁶

In our opinion, the change in resistance observed by Jakob and coworkers was due to secondary photoreactions. That phenomenon, in fact, was observed only in the case of very dilute solutions in which secondary photoreactions undoubtedly occurred after a few minutes of irradiation. This was shown by the fact that, under experimental conditions similar to those used by Jakob, *et al.*,^{7g} we observed that the pH increased only for a few minutes, and then it began to decrease.

A final point is worth discussing. Although our results clearly show that the primary photoreaction causes the release of CN^- , they do not prove that such a photoreaction is really photoreaction 1. In fact, reactions 4-6 can explain the zero-order law of formation of OH^- as well as reaction 1.²⁷ The occurrence of



reaction 6, however, can be ruled out since the primary product is a red species and not a blue one. On the other hand, to our knowledge, the simultaneous splitting off of more than one ligand has never been observed in photosubstitution reactions of coordination compounds. In particular, as far as the cyanide complexes are concerned, $\text{Co}(\text{CN})_6^{3-}$ ¹⁷ and $\text{Fe}(\text{CN})_6^{4-}$ ²⁸ are known to give a monosubstituted species as their primary photoproduct. Therefore, it seems plausible that the primary photoreaction of $\text{Mo}(\text{CN})_8^{4-}$ is really reaction 1.

Acknowledgment.—The authors are indebted to Professor V. Carassiti for his interest in this work and for his helpful criticism.

(25) It should also be considered that the $\text{M}(\text{CN})_8^{4-}$ ions always carry a number of water molecules during their migration.

(26) A quantum yield of 1 for photoreaction 2 has been assumed in this calculation; if a lower quantum yield is assumed, the difference in conductance would be higher (for example, 60% for $\phi = 0.2$).

(27) While the dissociation of the heptacyanoquo species $\text{Mo}(\text{CN})_7(\text{H}_2\text{O})^{3-}$ is certainly negligible at pH 6-7, under such conditions the actual form of the tetracyano complex is $\text{Mo}(\text{CN})_4(\text{O})(\text{OH})^{3-}$,¹⁰ and the predominant form of the hypothetical penta- and hexacyano species should be $\text{Mo}(\text{CN})_5(\text{OH})_2(\text{H}_2\text{O})^{3-}$ and $\text{Mo}(\text{CN})_6(\text{OH})(\text{H}_2\text{O})^{3-}$, respectively. Therefore, the quantum yield of OH^- formation should coincide with the quantum yield of the $\text{Mo}(\text{CN})_8^{4-}$ disappearance, independent of the actual formulation of the primary photosubstitution reaction.

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