The effect of sulfurhexafluoride on the photochemistry of aqueous anions.

Michael D. Crawford

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The Effect of Sulfurhexafluoride on the
Photochemistry of Aqueous Anions

by

Michael D. Crawford

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Submitted to the Faculty of Graduate Studies through
the Department of Chemistry in partial fulfillment
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Abstract

The effect of SF₆ on the 2537Å photolysis of aqueous I⁻, Fe(CN)₆⁻⁴ has been studied. The values $\xi(e^-aq) = 0.23$ for I⁻ and 0.36 for Ru(CN)₆⁻⁴ reported in the literature using N₂O were reproducible using SF₆ where $\xi(e^-aq) = \xi(F^-/6)$. Of the three values of $\xi(e^-aq)$ for Fe(CN)₆⁻⁴ (1.0, 0.66 and 0.35) previously published, neither the higher nor lower value could be duplicated however from three independent systems the mean value of $\xi(e^-aq) = 0.67 \pm 0.03$ was calculated.

From competition studies between SF₆ and N₂O the ratio $k_e + SF₆/k_e + N₂O = 2.0 \pm 0.2$ was determined thus confirming the specificity of SF₆ as a scavenger of $e^-aq$ in photochemical systems. A high molecular electron affinity in order to account for the reactivity towards $e^-aq$ of the otherwise inert SF₆ is proposed on the basis of a simple molecular orbital scheme. An overall mechanism for the reactions describing the effects of SF₆ as a scavenger of $e^-aq$ is given.

It is tentatively suggested that Ru(CN)₅N₂⁻³ is formed in the 2537Å photolysis of Ru(CN)₆⁻⁴ - N₂O - SF₆ solutions. Conclusive evidence for such a product could not be obtained, however, by virtue of the potential significance of such a species a speculative mechanism is proposed.

Both Pd(CN)₄⁻² and Pt(CN)₄⁻² were found to be photochemically inert with 2537Å radiation. This effect is interpreted as part of a general trend towards reduced photochemical activity with increasing covalency of the irradiated ion.
ACKNOWLEDGEMENT

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Introduction

1. General

Historically the major effort in photochemistry has involved photosynthesis of organic systems and it is only recently that aqueous inorganic systems have become the object of serious investigation. It may be rationalized that the development of aqueous inorganic photochemistry had to await the advent of modern instrumentation and the formulation of an adequate theoretical basis. For the simplest inorganic ions such as the halides, the absorption spectra in aqueous solutions occur in the region of 2300 Å to 1700 Å and thus many of the spectral details have only recently been interpreted. For the more complex ions such as the transition metal complexes, the readily accessible visible and near ultra-violet regions are often rich in spectral features; however, interpretation of these spectra requires a knowledge of crystal field or ligand field theory, neither of which were available to the chemist until relatively recently.

The ideal photochemical study would trace all the events from the initial act of photon absorption to the final establishment of thermodynamic equilibrium. While such a program is by no means impossible or at least should not be discouraged as an altruistic dream, it is rarely feasible to contemplate such a project when considered against the background of potential complexities. The establishment of absolute band assignments, which is in itself not infrequently extremely difficult or impossible, would seem to be an essential prerequisite. Unfortunately there is no guarantee that the excited state thus defined is the
immediate precursor to the chemically detectable intermediates or products. For example, the initial excited state could revert to a new state via intersystem crossing, undergo phosphorescence to a state of different multiplicity, alter its symmetry by a molecular rearrangement before ultimately dissociating to yield the first identifiable product. In such a case the spectra would provide few clues to the overall mechanism. On the other hand, many systems appear to exhibit a strong correlation between the excited state postulated from the spectral interpretation and the intermediates and products observed. Thus a detailed spectroscopic investigation can frequently be an invaluable aid, but need not be a prerequisite.

Just as a knowledge of the excited state may provide a basis upon which to explain or anticipate the existence of novel intermediates in photochemical mechanisms, the identification of such intermediates may lend credibility to some spectroscopic assignments. This is seen to be particularly true when the intermediate is a solvated electron and the initial excitation is assigned as a charge transfer to solvent (CTTS)\(^{(5,6)}\).

As a precaution it should be noted that the formation of solvated electrons does not necessarily require a CTTS transition as a precursor nor does the identification of a CTTS band guarantee the formation of solvated electrons. These points will be discussed in more detail later.

This thesis is primarily concerned with the identification and characterization of photochemically generated intermediates. In particular, the intermediate of primary concern is the solvated electron. This species in aqueous solution is known as a hydrated electron or
simply $e^{-}_{aq}$.

Prior to the early 1950's the suggestion that an electron could be solvolysed by water to form a stable species would not have been accorded serious consideration. However, a mounting series of anomalies in radiation chemistry (7) and the detailed calculations of Platzman (8) began to encourage researchers to regard the existence of $e^{-}_{aq}$ as possible or at least the subject of respectable conjecture. By the late 1950's there began a rapid accumulation of data to support the existence of $e^{-}_{aq}$ and in 1962 definitive kinetic experiments established that the $\gamma$-radiolysis of water produced a simple reducing species of unit negative charge (9), the hydrated electron. The final confirming evidence was provided by the observation in pulse radiolysis experiments of the transient absorption spectrum of the hydrated electron (10). Following these initial discoveries a vast amount of data has been accumulated about $e^{-}_{aq}$ (11) amongst which was the observation by flash photolysis that $e^{-}_{aq}$ was a primary product in the photolysis of a variety of aqueous inorganic anions (12).

Having established that $e^{-}_{aq}$ is a potential photochemical intermediate the subsequent problems to be solved were mainly how to correlate the excited state with the formation of $e^{-}_{aq}$ and how to detect and quantitatively measure the yields of $e^{-}_{aq}$.

Although flash photolysis represents a convenient means of detection, there are serious limitations involved in this technique. Firstly, absolute quantum yields (the number of species produced per quantum absorbed) can rarely be measured by this technique and secondly,
the lifetime of $e^{-}\text{aq}$ is a function of the solute composition of the solution and may be reduced beyond the limits of detection of the apparatus. Thus, it is frequently advisable to use a scavenger solute in quantitative work. The ideal scavenger should (a) be inert to all but the intermediate of interest and (b) yield a unique, inert and easily measurable product.

The molecule nitrous oxide ($N_2O$) is most frequently chosen as a scavenger for $e^{-}\text{aq}$ since it fulfills, though not perfectly, the criteria listed above. The reaction of $e^{-}\text{aq}$ with $N_2O$ is diffusion controlled:

$$e^{-}\text{aq} + N_2O \rightarrow N_2 + O^- (\text{+ } H_2O \rightleftharpoons OH + OH^-)$$

resulting in the formation of the inert molecule $N_2$ thereby satisfying condition (b). Since this reaction is diffusion controlled whilst the reaction of other reducing radicals with $N_2O$ are much slower (e.g. $k_{H+N_2O} \leq 10^5 M^{-1}s^{-1}$) condition (a) is approximately satisfied.

However, when the exciting radiation is of wavelength shorter than 2000 Å a direct photodissociation of $N_2O$ can occur. For example, aqueous $N_2O$ illuminated with 1849 Å light produces $N_2$ with $\delta(N_2) = 1.0$ thereby completely failing criterion (a). Thus, it is desirable to introduce an alternate to $N_2O$ particularly for use at shorter wavelengths.

It has been demonstrated recently that the molecule SF$_6$ can also be used as a scavenger of $e^{-}\text{aq}$ in both radiation chemistry and photochemistry. Besides being extremely inert, except to $e^{-}\text{aq}$ for which $k_{e+SF_6} = 1.65 \times 10^{10} M^{-1}s^{-1}$, SF$_6$ is transparent to ultraviolet radiation in the region of 1849 Å. Lacking in the
photochemical investigation of SF$_6$ as an electron scavenger were any kinetic studies to confirm its specificity towards e$^{-}$aq. Thus, this research program was undertaken to consider and examine in detail the kinetics and mechanisms involved in the reaction of e$^{-}$aq with SF$_6$.

The 2537Å photolysis of aqueous I$^{-}$ containing the competing solutes SF$_6$ and N$_2$O was chosen as a model since (a) the photolysis of aqueous I$^{-}$ has been thoroughly studied and should not present a source of anomalies, (b) the competing solutes are both neutral molecules thus eliminating the usual ionic strength corrections, (c) all the products of interest are easily and quantitatively measureable, and (d) both the absolute rate constants and relative rate constant ratios of e$^{-}$aq with SF$_6$ and N$_2$O have been measured by the methods of radiation chemistry.

A second system of interest is the 2537Å photolysis of Fe(CN)$_6^{3-}$ for while there can be no doubt that e$^{-}$aq is produced, three widely different values (1.0$^{(17)}$, 0.66$^{(18)}$ and 0.35$^{(19)}$) for $\phi$(e$^{-}$aq) have been reported. Since at least two of these values ($\phi$(e$^{-}$aq) = 0.66 and 0.35) were determined from very detailed studies of the Fe(CN)$_6^{3-}$ system the origin of the disagreement is not obvious. Although Waltz and Adamson$^{(20)}$ have also recently reported a value of $\phi$(e$^{-}$aq) = 0.66, thus supporting the results of Dainton and Air$^{(18)}$, it seemed appropriate to study the effect of SF$_6$ on the Fe(CN)$_6^{3-}$ system, hopefully to substantiate one or the other of the previously reported values and if possible elucidate the origin of the discrepancies.

The 2537Å photolysis of N$_2$O saturated Ru(CN)$_6^{3-}$ has been reported to yield $\phi$(N$_2$) = 0.36$^{(20)}$. Since Fe and Ru are congeners it is of
interest to confirm (in view of the uncertainties with Fe(CN)$_6^{4-}$) this yield, since a comparison of $\xi(e^{-}aq)$ for Fe(CN)$_6^{4-}$ and Ru(CN)$_6^{4-}$ could provide a useful insight into the processes determining the degradation of the respective excited states. At the same time Ru(CN)$_6^{4-}$ also provides an additional system with which to test the utility of SF$_6$. In any event, the photolysis of Ru(CN)$_6^{4-}$ solutions containing SF$_6$ and N$_2$O resulted in an unexpected and novel observation.

Finally, the two complexes Pt(CN)$_4^{-2}$ and Pd(CN)$_4^{-2}$ were irradiated with 2537$\AA$ light to explore the possibility of photochemical activity in these molecules. Both of these molecules were the object of detailed spectroscopic studies and there appears to be little agreement in the band assignments in the 2537$\AA$ region. As indicated earlier, the photochemistry of a molecule constitutes an extremely tenuous basis for a band assignment; however, the hope here was that a clue might be provided in an otherwise ambiguous situation.

2. Excitation Processes

The anions of interest in this investigation can be divided into two classes (a) monatomic anions and (b) anionic transition metal complexes. It seems appropriate to describe at least briefly the probable excitation processes which would contribute to the ultraviolet photochemistry of these ions.

2.1 Charge Transfer to Solvent (CTTS)

The ultra-violet absorption spectra of ions such as Cl$^-$, Br$^-$, and I$^-$ are strongly characterized by their sensitivity to solvent perturbations. Furthermore, each spectra in this series exhibits a doublet
structure of the magnitude of the splitting of the $^2P_{1/2}$ and $^2P_{3/2}$ states of the respective halogen atoms. Thus the appearance is given that the halide ($X^-$) transfers its charge to the solvent (thus the solvent dependence) with the resultant formation of the halogen atom (thus the correlation with the $^2P$ ground state of the atom). Since the photochemical result is the generation of $e^{-aq}$ this description would seem adequate; however, as such it fails on energetic grounds alone. If the process is only as described above, then the energetics of electron ejection into the bulk of the solvent is given simply by the electron affinity of the halogen. In the case of $I^-$ this is $24,650 \text{ cm}^{-1}$ whereas the first absorption maximum is at $44,200 \text{ cm}^{-1}$, clearly then this model includes the solvent molecules as part of the total ensemble constituting the ground state of the ion. Thus, the energy of the ground state is given not only by the electron affinity of the halogen but also by a Madelung like term comprising the solvent-solute interaction energy $^{(2,3)}$. Excitation of this species results in a high energy configuration of the ion in which the charge is now localized on the primary solvent shell rather than the valence orbitals of the halogen.

The ensuing photochemical activity (i.e. $e^{-aq}$ formation) measures the fate of this excited state. $\phi (e^{-aq})$ decreases in the series $\text{Cl}^-$, $\text{Br}^-$ and $\text{I}^-$ $^{(16)}$ which is the opposite to that expected in terms either of extinction coefficient or electron affinity. However, within the excited state there will be a repulsion between the charge configuration of the halogen-like component and the charge localized on the solvent. This repulsion will be a maximum for the least polarizable halogen and a minimum for the most polarizable. Furthermore, the separation of the
halogen and the charged solvent shell requires diffusion out of the shell by the halogen and a smaller halogen (i.e. Cl) will diffuse more rapidly than the larger one (i.e. I).

In terms of this model, it is seen that the term CTTS is more appropriate to the overall process than to the excitation.

2.2 Charge Transfer Ligand to Metal (CTLM)

The molecular orbital model of transition metal complexes is derived by taking linear combinations of metal and ligand orbitals \(^{23,24}\). The bonding orbitals thus constructed are localized essentially on the ligands and the low-lying anti-bonding orbitals are primarily localized on the metal. An excitation involving an electron from either a \(\sigma\) or \(\pi\) bonding orbital to a \(\sigma^*\) or \(\pi^*\) anti-bonding orbital (presuming the transition to be allowed) can thus be described as a charge transfer from the ligand to the metal. Since the molecular orbitals are neither pure ligand nor metal orbitals the term CTLM is obviously not meant to be interpreted literally. The dominant consequence of this type of excitation is photohydrolysis since the effective reduction in bond order facilitates the normal unimolecular hydrolysis mechanism. Solvated electron formation from a CTLM excitation has never been reported.

2.3 Charge Transfer Metal to Ligand (CTML)

Where there is an intramolecular \(\pi\)-bonding system within the ligand (e.g. CO or CN\(^-\)) there must also be a \(\pi^*\)-antibonding orbital. The symmetry of such orbitals have the same transformation properties as certain of the metal orbitals (depending on the symmetry point group)\(^ {25}\). Thus, some of the otherwise high energy molecular antibonding orbitals
will be reduced in energy due to orbital overlap with the ligand antibonding orbitals. The effect then is to bring into the normal spectroscopic region (30,000 cm\(^{-1}\) to 60,000 cm\(^{-1}\)) transitions from molecular orbitals localized on the metal to orbitals localized on the ligand. Again, the designation CTML is not formal.

A variety of photochemical consequences can result, one of which is the formation of solvated electrons. The precise mechanism is unknown and certainly that proposed for the simple halides would hardly seem suitable here. However, by localizing the charge in a ligand antibonding orbital this electron will experience a markedly reduced nuclear attraction, (the extent of which will depend on the degree of localization defined by the wave-function for the excited state). It then becomes possible for the solvent to provide a greater potential well for the electron than that represented by the excited state; thus, \(e^{-}_{aq}\) might result.

3. The Reactions of \(e^{-}_{aq}\) with SF\(_6\)

Asmus and Fendler (15, 26, 27) have reported several studies involving the use of SF\(_6\) in radiation chemistry. The essential features of their work are (a) the absolute rate constant for the reaction of \(e^{-}_{aq}\) with SF\(_6\) is \(k_{e+SF_6} = 1.65 \times 10^{10} M^{-1} S^{-1}\), (b) the stoichiometry is given by: \(e^{-}_{aq} + SF_6 \rightarrow 6F^- , 8H^+ , SO^=\) and (c) SF\(_6\) is a specific scavenger of \(e^{-}_{aq}\) under the conditions employed.

Prior to this work the only photochemical studies reported (16) involving the use of SF\(_6\) in aqueous solution, established for the 2537\(\AA\) photolysis of I\(^-\) and the 1849\(\AA\) photolysis of Cl\(^-\), Br\(^-\), HPO\(^=\), SCN\(^-\) and H\(_2\)O that the yield relationship \(\xi(\cdot/F^-/6) = \xi(e^{-}_{aq})\) is valid and that

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\( \text{SF}_6 \) is transparent to 1849Å radiation. No kinetic details were reported nor was an explanation proposed for the apparent specificity of \( \text{SF}_6 \) for \( \text{e}^-\text{aq} \).
Experimental

1. Materials

The solutions were prepared with water which had been distilled from acid dichromate in a stream of oxygen over a hot platinum filament, condensed and redistilled from alkaline permanganate and maintained under constant reflux over alkaline permanganate.

The salts FeCl$_3$, K$_3$Fe(C$_2$O$_4$)$_3$, KF, KCl, KBr, KI, Na$_2$HPO$_4$·12H$_2$O and K$_4$Fe(CN)$_6$·3H$_2$O were reagent grade and were used without further purification. The chemicals such as K$_4$Ru(CN)$_6$·3H$_2$O [Alfa Inorganics], K$_2$Pd(CN)$_4$ [K and K Laboratories Inc.], K$_2$Pt(CN)$_4$ [Research Inorganic Chemical Co.] used, were of the purest grade available.

The gases N$_2$O and SF$_6$ [The Matheson Company] were purified by repeated trap to trap distillations, stored in the vacuum system and redistilled several times just prior to use.

2. Apparatus and Procedure

The two standard photolysis vessels used consisted of (a) a cylindrical optical grade high purity quartz cell 20 mm in depth to which was attached a 100 ml degassing bulb and a 10 mm pathlength spectrophotometer cell (see figure 1), (b) a rectangular optical grade high purity quartz cell 20 mm in depth to which was attached a 50 ml degassing bulb and a 10 mm pathlength spectrophotometer cell (see figure 2).

The reaction vessels were cleaned with permanganic acid, rinsed with water then rinsed with a solution of nitric acid and hydrogen peroxide. The cell was then thoroughly rinsed with triple-distilled water followed by quadruple-distilled water.
Figure 1
Figure 1

Photochemical Cell (a)

A = high purity quartz compartment.
B = teflon coated stirring bar.
C = 10 mm pathlength quartz spectrophotometer cell with a graded quartz pyrex seal.
D = 100 ml degassing bulb.
E = a 14/35 standard taper joint to which a stop-cock could be joined for connecting to the vacuum system.
Figure 2

Photochemical Cell (b)

A = high purity quartz compartment.
B = teflon coated stirring bar.
C = 10 mm pathlength quartz spectrophotometer cell with a graded quartz pyrex seal.
D = 50 ml degassing bulb.
E = a 14/35 standard taper joint to which a stop-cock could be joined for connecting to the vacuum system.
The solutions were pipetted into the vessel through a side arm to which a stop-cock could be joined for connecting to the vacuum system. After thorough deaeration, the solutions were equilibrated with the desired partial pressure of SF$_6$ or N$_2$O or both. When using the mixed gases the procedure was as follows - after the sample solution was equilibrated with the desired partial pressure of SF$_6$, the latter was then removed and stored in a bulb at -196°C; the sample was then equilibrated with the desired partial pressure of N$_2$O and then frozen with liquid nitrogen; the SF$_6$ was then distilled back into the sample; the sample vessel was then removed from the vacuum system and thawed.

Since the pressure of the additive gases was measured with a mercury manometer, the solutions were protected from contamination by mercury vapour by placing a trap (CO$_2$-acetone with N$_2$O and ice-salt slurry with SF$_6$) between the manometer and the reaction vessel.

The photochemical lamp used with cell (a) was an Oriel model C-13-62 low pressure mercury lamp and with cell (b) a model PCQ011S low pressure mercury grid lamp (Ultra Violet Products, Inc., San Gabriel, California). For most experiments both lamps were used in conjunction with a stabilized power supply.

In the irradiations with the 2537Å line reaction cell (a) was immersed in a constant temperature water bath (25 ± 2°C) with the radiation passing through a quartz window; reaction cell (b) was placed in a fixed position relative to the lamp and a water filter inserted between the reaction cell and the lamp. Both cells contained teflon coated magnetic stirring bars and all solutions were vigorously stirred.
during irradiation.

The intensity of the $2537\text{Å}$ line was determined by a differential actinometric method using a ferric oxalate actinometer\(^{(30)}\). As a further precaution to assure the constancy of intensity, the actinometry was repeated immediately before and after each run.

The spectrophotometric results were obtained using both a Beckman DK-1A far u.v. and a Beckman DB recording spectrophotometer. In some instances these determinations were simply accomplished by allowing the photolysed sample to flow directly into the spectrophotometer cell C, shown in figure 1 and 2. In other cases a portion of the photolysed sample was removed and analysed using a standard cuvette. All spectrophotometric determinations were made using reagent blanks.

The iodine yields were measured as $\text{I}_2^-$ using the spectrophotometric absorption at $353\text{mμ}$ and the extinction coefficient $2.64 \times 10^4 \text{M}^{-1}\text{cm}^{-1}$. The total iodine yield is given by the sum $\text{I}_2 + \text{I}_3^-$ where $\text{I}_2$ was calculated using $742 \text{M}^{-1}$ as the equilibrium constant for $\text{I}^- + \text{I}_2 \rightleftharpoons \text{I}_3^-$. The absorption at $420 \text{mμ}$ with $\varepsilon_{420} = 1.03 \times 10^3$ was used to calculate the Fe(CN)$_6^{3-}$ yields.

Fluoride and cyanide were measured by means of an Orion specific ion electrode with an Orion model 801 meter. The calibration curves were obtained using standard solutions in reagent blanks. In the case of CN$^-$ the solutions were made 0.1 N NaOH to prevent hydrolysis.

Gaseous products were analyzed by removal from the reaction cell by successive freeze-pump-thaw cycles and injection into a Varian model 1521-B chromatograph employing a molecular sieve 13X column.

PH readings were measured using a Sargent Model DR pH meter.
Results

A) Photolysis of I⁻ Solutions: Containing SF₆ and N₂O

The products measured after irradiation with 2537Å light of aqueous 5 x 10⁻² M I⁻ solutions containing SF₆ and N₂O were N₂, I₂ (I⁻) and F⁻, the yields of which were linear with time for the irradiation times used. The total iodine yield is given by the sum \( \phi(I_2 + I_3) \) which for convenience will be represented by \( \phi(I_2) \). The relationship between the yields were \( \phi(I_2) = \phi(N_2) \) and \( \phi(e^{−}aq) = \phi(F^{−}/6) + \phi(I_2) \), where \( \phi(e^{−}aq) \) has been determined from I⁻ solutions containing only SF₆ or N₂O at an equivalent concentration. The relative yields of F⁻ and I₂ (reaction [2] and [3]) depend upon the competition for e⁻aq produced by reaction (1)

\[
\begin{align*}
I^- + h\nu (2537\AA) &\rightarrow e^{−}aq + I \\
e^{−}aq + SF_6 &\rightarrow 6F^{−}, SO_4^{−}, 8H^+ \\
e^{−}aq + N_2O &\rightarrow N_2, I_2, 2OH^- 
\end{align*}
\]

Under the conditions used in the experiments reaction [3] always predominated, thus preventing a sufficient increase in \([H^+]\) to suppress the apparent F⁻ yield. Accordingly, the pH of the post irradiated solutions were found to be near neutral or slightly alkaline. The usual linear equation used to describe the competition between N₂O and SF₆ for e⁻aq
requires that $\phi(e^{-}\text{aq})$ be constant over the range of scavenger concentrations employed, a condition not satisfied by the concentrations employed here ($[\text{SF}_6] = 1.8 \times 10^{-4}\text{ M}$ and $[\text{N}_2\text{O}] = 1.0 \times 10^{-3}$ to $3\times10^{-3}\text{ M}$ for which $\phi(e^{-}\text{aq})$ is known to vary). By combining equation (1) with the equivalent equation for $\phi(I_2^-)$ it is easily shown that the yield ratio is given by equation (2).

$$\frac{\phi(F^-/6)}{\phi(I_2^-)} = \frac{k_2}{k_3} \frac{[\text{SF}_6]}{[\text{N}_2\text{O}]}$$ (2)

The rate constant ratios listed in Table 1 have been computed in this way. It can be seen from the table that the mean value taken from six runs was $k_2/k_3 = 2.00 \pm 0.2$. The effect of added salts on $[\text{I}^-] = 1 \times 10^{-2}\text{ M}$ solutions containing $[\text{SF}_6] = 1.8 \times 10^{-4}\text{ M}$ and $[\text{N}_2\text{O}] = 1.8\times10^{-3}\text{ M}$ was tested using $4 \times 10^{-2}\text{ M}$ of $F^-$, $\text{Cl}^-$ and $\text{Br}^-$ respectively. The yields from these solutions including the $5 \times 10^{-2}\text{ M}$ $\text{I}^-$ solution differed by less than 3% indicating no significant effect. Table 1 shows that $k_2/k_3$ is independent of ionic strength and within the limits of experimental error these values are in excellent agreement with ratios calculated from the absolute rate constants or measured by the $\gamma$-radiolysis of aqueous $\text{SF}_6 - \text{N}_2\text{O}$ solutions\(^{15}\).

(B) **Photolysis of Aqueous Transition Metal Anionic Complexes**

1. **$\text{Fe(CN)}_{6}^{4-} - \text{N}_2\text{O}$ Solutions**

The products measured on photolysis of aqueous $3.5 \times 10^{-3}\text{ M} \text{Fe(CN)}_{6}^{4-}$
Table 1

<table>
<thead>
<tr>
<th>e⁻aq origin</th>
<th>Ionic strength</th>
<th>k₂/k₃</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2537 Å photolysis</td>
<td>0.05</td>
<td>2.00±0.2</td>
<td>This work</td>
</tr>
<tr>
<td>I⁻</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2537 Å photolysis Fe(CN)₆⁴⁻</td>
<td>3.5x10⁻³*</td>
<td>2.20±0.2⁺</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.85±0.2⁺</td>
<td></td>
</tr>
<tr>
<td>Y-radiolysis</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>0</td>
<td>1.75₃</td>
<td>(15)</td>
</tr>
<tr>
<td>pulse radiolysis</td>
<td>0</td>
<td>1.92±0.27</td>
<td>(15) (13)</td>
</tr>
</tbody>
</table>

* Degree of dissociation of K₄Fe(CN)₆ is unknown
⁺ Obtained using equation (2)
⁻ Obtained using equation (1)
₃ Error limits not quoted.
solutions containing \([N_2O] = 2 \times 10^{-2} \text{M}\) were \(N_2\), \(Fe(CN)_6^{3-}\) and a relatively low yield of \(CN^-\). Using an aqueous KI filter to remove the 2537\(\AA\) line, resulted in no formation of \(N_2\) or \(Fe(CN)_6^{3-}\); however, the yield of \(CN^-\) was virtually unaffected. These observations are consistent with the results of Ohno (31) who has shown that photohydrolysis is the dominant process at exciting wavelengths longer than 2537\(\AA\). In any event, the formation of \(Fe(CN)_5^{5-}H_2O^{3-}\) implied by the yield of \(CN^-\) would be too low to effect an error in the determination of \(Fe(CN)_6^{3-}\) whose spectrum overlaps \(Fe(CN)_5^{5-}H_2O^{3-}\) at the analytical wavelength employed.

From linear yield versus time plots the relationship and average yield due to photolysis by the 2537\(\AA\) line was found to be 

\[\Phi(Fe(CN)_6^{3-}) = \Phi(N_2) = 0.64 \pm 0.04\] and independent of the lamp intensity over the range \(2 \times 10^{-4}\) to \(6 \times 10^{-6}\) einsteins/l/min. These results are in excellent agreement with Dainton and Airey (18) and Waltz and Adamson (20).

The quantum yield of nitrogen was independent of the irradiation time and when the \(Fe(CN)_6^{3-}\) yields were measured prior to the gas analysis, linear yield versus time plots were obtained. The lower yields of Ohno (19) could not be reproduced, although it was observed that the repeated freeze-thaw cycles employed in the gas analysis caused a substantial reduction (\(\sim 30\%\)) in the optical density at 420 \(\mu\)m of the photolysed solutions, however, on standing the optical density slowly increased approaching its original value.

\[\text{(II) } Fe(CN)_6^{3-} - SF_6 \text{ Solutions} \]

The variation of the \(F^-\) yield with irradiation time for the 2537\(\AA\) photolysis of \(5 \times 10^{-3}\) \(\text{M} \ Fe(CN)_6^{3-}\) solutions containing \([SF_6]^-\)
Figure 3
The dependence of $F^-$ yields on the irradiation time at the intensity of $1.24 \times 10^{-4}$ einstein $\cdot$ min$^{-1}$ in the 2537Å photolysis of aqueous Fe(CN)$_6^{4-}$ containing $[SF_6] = 1.9 \times 10^{-4} \text{M}(0)$ and $1.4 \times 10^{-3} \text{M}(0)$. 

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Figure 4

The variation of $\delta(F^-)$ with [SF$_6$] in the 2537Å photolysis of Fe(CN)$_6^{4-}$. 
1.4 \times 10^{-3} \text{M} to 1.9 \times 10^{-4} \text{M} is shown in figure 3. The pronounced curvature in the F\(^-\) yields when [SF\(_6\)] < 10^{-3} \text{M} is easily understood in terms of depletion of [SF\(_6\)] as well as the competition for e\(^-\)aq by the product ions Fe(CN)\(^{3-}\)/6 and H\(^+\) (the latter being indicated by a decrease in pH). Figure 4 illustrates the dependence of $\psi(F^-)$ on [SF\(_6\)] where $\psi(F^-)$ has been determined from the initial linear part of plots such as those in figure 3. When [SF\(_6\)] < 10^{-4}, the yield versus time plots showed a continuous curvature precluding an accurate determination of $\psi(F^-)$; thus, these values of $\psi(F^-)$ are necessarily only approximate.

Using the plateau value of figure 4 and assuming the 1:6 ratio between e\(^-\)aq and F\(^-\) found for other systems\(^{16}\), then $\psi(e^-\text{aq}) = \psi(F^-/6) = 0.69 \pm 0.02$. In contrast to the Fe(CN)\(^{-4}\)/6 — N\(_2\)O systems, the CN\(^-\) yields from the photolysis of Fe(CN)\(^{-4}\)/6 — SF\(_6\) solutions were relatively large (i.e. ~50% of the F\(^-\) yield). The CN\(^-\) yields did not appear to show a systematic dependence on the irradiation time and it was subsequently found that the yield was due to processes initiated not only by the 2537\(\AA\) line but also by the longer wavelengths emitted by the lamp and furthermore, that a substantial fraction was formed in the post-irradiation period. At least one consequence of these relatively large CN\(^-\) yields is that it can no longer be assumed that the pentacyanomonoaquoferrate (II) will not contribute to the absorbance at 420 m\(\mu\). If only Fe(CN)\(^{-3}\)/6 is assumed to be absorbing at 420 m\(\mu\), then the apparent yield when [SF\(_6\)] = 1.4 \times 10^{-3} \text{M} would be $\psi(\text{Fe(CN)}^{-3}/6 = 1.9 \pm 0.10$. If $\psi(e^-\text{aq}) = \psi(F^-/6) = \psi(\text{Fe(CN)}^{-3}/6)/2$, then the ratio $\psi(F^-)/\psi(\text{Fe(CN)}^{-3}/6)$ should be 3.0, however,
values ranging from 2.5 to 1.7 were obtained depending upon \([\text{SF}_6]\) and irradiation time. It is clear that under these conditions, the absorbance at 420 m\(\mu\) does not provide a reliable measurement of \(\text{Fe(CN)}_6^{3-}\).

(III) \(\text{Fe(CN)}_6^{-4} - \text{N}_2\text{O} - \text{SF}_6\) Solutions

Solutions in which \([\text{Fe(CN)}_6^{-4}] = 5 \times 10^{-3}\text{M}\) and containing \(\text{N}_2\text{O}\) in the range \([\text{N}_2\text{O}] = 8.6 \times 10^{-4}\) to \(2.9 \times 10^{-3}\text{M}\) and \([\text{SF}_6] = 1.8 \times 10^{-4}\text{M}\) were photolysed. In conjunction with these experiments but reported elsewhere (32) a series of \(\text{Fe(CN)}_6^{-4}\) solutions containing \([\text{N}_2\text{O}] = 1.5 \times 10^{-2}\text{M}\) and \([\text{SF}_6] = 1.8 \times 10^{-4}\) to \(1.4 \times 10^{-3}\text{M}\) were photolysed. Since with these latter solutions the sum \((\text{[N}_2\text{O}] + \text{[SF}_6])\) was sufficiently large to ensure that \(\xi(e^{-}\text{aq})\) would be constant, then equation [1] was applicable. The appropriate plot is depicted in figure 5 from which the values \(\xi(e^{-}\text{aq}) = \xi(F^{-}/6) = 0.67 \pm 0.05\) and \(k_2/k_3 = 1.85 \pm 0.2\) were calculated from the intercept and slope respectively. For the lower values of \([\text{SF}_6]\) and \([\text{N}_2\text{O}]\) (for the reasons given with the I system), it is best to use equation [2]. Using the data from nine experiments with \([\text{SF}_6] = 1.8 \times 10^{-4}\text{M}\) and \([\text{N}_2\text{O}]\) in the range \(8.6 \times 10^{-4}\) to \(2.9 \times 10^{-3}\text{M}\) resulted in \(k_2/k_3 = 2.20 \pm 0.20\). Since the pH of these solutions remained near neutral and the CN\(^-\) yields were comparable to those for the \(\text{Fe(CN)}_6^{-4}\cdot\text{N}_2\text{O}\) system, the absorbance at 420 m\(\mu\) was assumed to provide an acceptable measure of \(\text{Fe(CN)}_6^{3-}\). The yield relationship was found to be \(\xi(\text{N}_2^0) + \xi(\text{F}^{-}/6) = \xi(\text{Fe(CN)}_6^{3-}/2)\).

(IV) \(\text{Ru(CN)}_6^{-4} - \text{N}_2\text{O}\) Solutions

Solutions in which \([\text{Ru (CN)}_6^{-4}] = 1.0 \times 10^{-2}\text{M}\) and containing \(\text{N}_2\text{O}\) in the range \([\text{N}_2\text{O}] = 1.11 \times 10^{-3}\) to \(1.90 \times 10^{-2}\text{M}\) were photolysed.
Figure 5

The effect on \( \delta(F^\cdot/6) \) of varying \([N_2O]/[SF_6]\)
in the 2537 Å photolysis of aqueous \(Fe(CN)_6^{4-}\)
in which \([N_2O]+[SF_6]>10^{-3} M\)
The only gaseous product was $N_2$, the quantum yield of which was independent of the irradiation time. The likely solution product, $\text{Ru(CN)}_6^{3-}$, could not be identified; however, an absorption band centered at 310 m$\mu$ was produced and increased as a linear function of time. The origin of this band could not be established.

At $[N_2O] = 1.11 \times 10^{-3}$ M, $\xi(N_2) = 0.25 \pm 0.02$ but increased with increasing $[N_2O]$. The value at $[N_2O] = 2.0 \times 10^{-3}$ M was $\xi(N_2) = 0.37 \pm 0.02$ and at $[N_2O] = 1.9 \times 10^{-2}$ M was $\xi(N_2) = 0.38 \pm 0.02$ which should represent the limiting value. This latter value is in close agreement with that of Waltz and Adamson (20).

V) $\text{Ru(CN)}_6^{4-} - N_2O - \text{SF}_6$ Solutions

Irradiation with 2537Å light of solutions containing $[\text{Ru(CN)}_6^{4-}] = 1 \times 10^{-2}$ M with $N_2O$ in the range $0.89 \times 10^{-3}$ to $2.86 \times 10^{-3}$ M and $[\text{SF}_6] = 1.75 \times 10^{-4}$, were carried out. Applying equation [2] to the data obtained resulted in $k_2/k_3 = 1.79 \pm 0.25$. It can also be seen from table 2 that within the limits of experimental error an acceptable material balance was obtained.

The determination of the $N_2$ yields from these solutions was complicated by an anomalous difficulty in extracting the $N_2$ from the photolyzed sample. Ordinarily, the freeze-pump-thaw cycle need only be applied three times to quantitatively remove $N_2$ from an irradiated sample with approximately 95 - 99% being taken in the first two cycles. However, with the $\text{Ru(CN)}_6^{4-} - N_2O - \text{SF}_6$ solutions at least nine cycles were required to effect an apparent complete extraction of the $N_2$. In order to test the analysis system, blanks were introduced (photolyzed KI - $N_2O$, $\xi(N_2) = 0.23$ and $\text{Ru(CN)}_6^{4-} - N_2O$, $\xi(N_2) = 0.38$) periodically,
Table 2

<table>
<thead>
<tr>
<th>Time (mins.)</th>
<th>$[SF_6]$</th>
<th>$[N_2O]$</th>
<th>$k_{SF_6}/k_{N_2O}$</th>
<th>$\frac{\delta(F^-/6) + \delta(N_2)}{e^{-}} = g(e^{-})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.76x10^{-4}</td>
<td>0.89x10^{-3}</td>
<td>1.72±0.2</td>
<td>0.06±0.19 = 0.25±0.03</td>
</tr>
<tr>
<td>30</td>
<td>1.75x10^{-4}</td>
<td>1.94x10^{-3}</td>
<td>1.35±0.2*</td>
<td>0.03±0.24 = 0.27*</td>
</tr>
<tr>
<td>10</td>
<td>1.76x10^{-4}</td>
<td>2.03x10^{-3}</td>
<td>1.62±0.2</td>
<td>0.040±0.29 = 0.33±0.03</td>
</tr>
<tr>
<td>10</td>
<td>1.75x10^{-4}</td>
<td>2.85x10^{-3}</td>
<td>2.04±0.2</td>
<td>0.03±0.31 = 0.34±0.03</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td></td>
<td></td>
<td>1.79±0.25</td>
</tr>
</tbody>
</table>

* low values are the result of solute depletion due to excessive irradiation time.
establishing the absence of an instrumental problem. This unusual
behaviour suggested that the product N₂ in the photolyzed Ru(CN)₆⁻₄ -
N₂O - SF₆ may have been fixed in a complex such as Ru(CN)₅N₂⁻³. Apart
from the usual absorption band at 310 μm no spectroscopic features
could be found to confirm the existence of such a species.

Since the decompositions of SF₆ is accompanied by an increase in
\[ [H^+] \] in unbuffered solutions, Ru(CN)₆⁻⁴ solutions at pH = 1.7 and pH = 5.75
with \[ [N₂O] = 2 \times 10^{-2} \text{M} \] were photolyzed. Whilst \( \xi(N₂) \) was reduced in
the first case due to the competition by \( H^+ \), \( \delta(N₂) \) in the latter case
was unchanged and in both cases the N₂ analysis was completely normal.
Thus, the origin of the anomaly in the N₂ analysis with the Ru(CN)₆⁻⁴ -
N₂O - SF₆ solution remains obscure.

VI) Pt(CN)₄²⁻ and Pd(CN)₄⁻² - N₂O Solutions

Solutions in which \[ [M(CN)]⁻₂ \] = 1 \times 10⁻³ \text{M} (where M=Pt or Pd)
and N₂O in the range \[ [N₂O] = 2.04 \times 10⁻³ \text{M} \text{ to } 1.91 \times 10⁻² \text{M} \] were irradiated
with 2537 Å light.

Even with extremely long exposure times it was impossible to
determine a N₂ yield beyond that of a reagent blank. Likewise, virtually
no CN⁻ could be detected indicating no photochemical activity upon
absorption of 2537 Å light for either complex.
Discussion

The values calculated for \( k_2/k_3 \) obtained from the photolyses of either aqueous \( I^- \) or \( Fe(CN)_6^{4-} \) containing \( SF_6 \) and \( N_2O \), are seen to be in good agreement with those obtained by radiation chemical techniques (table 1). The independence of \( k_2/k_3 \) to ionic strength is predictable on the basis of the Brønsted-Bjerrum theory; however, a specific ion effect which might have been anticipated was also absent. The absorption maximum of \( e^-_{aq} \) has been shown to be sensitive to both a change of solvent and added non-reactive solutes\(^{(33)}\). These effects are characteristic of a charge transfer to solvent (CTTS) excitation process and the band maximum should thus be related to the 'ionization potential' of \( e^-_{aq} \). If the energetics of the reaction

\[
e^-_{aq} + A \rightarrow A^-
\]  

are regarded as being largely defined by the difference in the ionization potential of \( e^-_{aq} \) and the electron affinity of \( A \), then it might be reasonable to expect a dependence of \( k_{e^-_{aq}+A} \) on the specific ionic atmosphere. In fact Anbar and Hart\(^{(33)}\) have presented data for reaction [3], which would appear to confirm such an effect. Unfortunately, these authors make no comment about the reduced solubility of \( N_2O \) in salt saturated solutions and by taking account of published solubility data\(^{(34)}\), a substantial reduction in \([N_2O]\) is to be expected. Thus, it is uncertain whether the reported effect on reaction [3] is due to a reduction in \([N_2O]\) or \(k_3\). In any event, for the photochemical systems studied \( k_2/k_3 \) was independent of the specific ionic atmosphere. It must be noted, however, that the solute concentration may not have been sufficiently
high to develop the potential effect, as a result the invariance observed cannot be assumed to be conclusive.

Over the range of \([N_2O]\) and \([SF_6]\) studied, the following material balance equations were satisfied:

\[
\xi(e^{-aq}) = \xi(F^-/6) + \xi(I_2) = \xi(N_2)
\]

\[
\xi(e^{-aq}) = \xi(F^-/6) + \xi(N_2) = \xi(Fe(CN)^{-3})/2
\]

and since \(Ru(CN)^{-3}\) could not be identified, only the simple relationship

\[
\xi(e^{-aq}) = \xi(F^-/6) + \xi(N_2)
\]

can be used with \(Ru(CN)^{-4}\). The evidence clearly confirms the relationship \(\xi(e^{-aq}) = \xi(F^-/6)\), despite the fact that in the \(I^-\) system there is no net oxidation while in the \(Fe(CN)^{-4}\) system, an overall oxidation of the \(Fe(CN)^{-4}\) is indicated and which is equivalent to that obtained in the presence of \(N_2O\) alone.

The average value, from the independent determinations(\(\xi(N_2)\)) from \(N_2O\) saturated solutions, \(\xi(F^-/6)\) from solutions in which \([SF_6] = 2 \times 10^{-3} M\) and the intercept of the competition plot) \(\xi(e^{-aq}) = 0.67 \pm 0.03\), for the 2537\(\AA\) photolysis of \(Fe(CN)^{-4}\) provides convincing support for the value reported by Dainton and Airey\(^{18}\). The erratic results for the apparent \(Fe(CN)^{-3}\) yields would seem best interpreted in terms of post-irradiation hydrolysis, caused at least in part by the effects
of the freeze-thaw cycles employed in the gas analysis procedure. With the Fe(CN)$_6^{3-}$ - SF$_6$ solutions, an acidic solution (pH ~ 5) is produced and the liberated CN$^-$ will be converted to HCN thus inhibiting the normal anation reaction. Although the data is insufficient to warrant a detailed interpretation of the various effects observed, it seems a fair conclusion that the 'Fe(CN)$_6^{3-}$ yields' do not constitute a totally reliable measure of $\xi(e^{-}_\text{aq})$. The potential error introduced in this way would still not account for the low yields reported by Ohno$^{(19)}$ and this discrepancy remains unresolved.

The special advantage of the use of SF$_6$ is in the quantitative relationship $\xi(e^{-}_\text{aq}) = \xi(F^-)/6$, and in its specificity towards $e^{-}_\text{aq}$. Even hydrogen atoms fail to react with SF$_6$, suggesting that its reactions are kinetically controlled. An apparent exception to the inert character of SF$_6$ is the reaction with exploding metals$^{(35)}$. While seemingly unrelated the similarity between these latter 'reagents' and a solvated electron is in their low ionization potentials suggesting that reaction with SF$_6$ is an electron transfer process determined in part by the high electron affinity of SF$_6$ and the low ionization potential of the donor species. Figure 6 represents a qualitative molecular orbital diagram of SF$_6$ based on orbital transformation properties in $O_h$ symmetry. For simplicity, the core approximation is made for the fluorine 2S electrons, leaving a $F^5$ valence configuration for fluorine. It can be seen, that the valence 3S and 3P electrons of sulfur could become localized on the fluorine principally through the $A_{1g}$ and $t_{1u}(\sigma)$ orbitals. Hypothetically, this would leave the sulfur in an extremely
Figure 6
Figure 6

Molecular orbital scheme for $\text{SF}_6$ based on the orbital transformation properties in $\text{Oh}$ symmetry.
electron deficient state, thus some balancing of charge would be required and can conveniently be visualized as involving the $t_{1u}$ and $t_{2g}\left(\pi\right)$ molecular orbitals. This partial withdrawal of charge from the fluorine through the $\pi$ bonds would be augmented if there was a contraction of the non-bonding $t_{1g}$ and $t_{2u}$ orbitals to reduce the effective nuclear charge of the fluorine. Such a scheme describes $SF_6$ with effectively no accessible lone pairs which would account for its lack of any discernable nucleophilic character, extremely low solubility and generally inert character. In particular this marked reduction in the availability of fluorine electrons would inhibit the formation of a transition state in possible highly exothermic abstraction reactions with reagents such as hydrogen atoms. On the other hand this scheme also describes the fluorines as being relatively electron deficient as compared to $F^-$ thus causing an overall high molecular electron affinity.

Further reference to figure 6 shows that the addition of an electron to $SF_6$ to yield $SF_6^-$ would involve use of a high energy antibonding orbital (presumably the $eg\left(\pi^*\right)$ or $t_{2g}\left(\pi^*\right)$) thus destabilizing the molecule. Dissociation of $SF_6^-$ could follow a variety of paths, however, maximum $\pi$ bonding and bond order would be maintained by the dissociation process

$$e_{aq}^- + SF_6 \rightarrow SF_6^- \quad [5a]$$

$$SF_6^- \rightarrow SF_5^- + F^- \quad [5b]$$

where $SF_5^-$ would have a trigonal bipyramidal geometry. The reaction
of SF$_5$ with an oxidizable substrate might simply parallel that proposed for SF$_6$

\[
\text{i.e. } SF_5 + A^- \rightarrow SF_5^- + A \quad [6a]
\]

\[
SF_5^- \rightarrow SF_4 + F^- \quad [6b]
\]

resulting in SF$_4$ which also has a trigonal bipyramidal structure$^{(37)}$, the lone pair being in the trigonal plane. Reactions $[5b]$ and $[6b]$ are not meant to imply the existence of SF$_6^-$ or SF$_5^-$ as intermediates, as these species may be in repulsive states, in which case, reactions $[5a]$ and $[5b]$ and $[6a]$ and $[6b]$ would constitute single concerted reactions.

The hydrolysis of SF$_4$ has been found to yield SOF$_2$(35) which further hydrolyses to SO$_3^-$. In systems such as I$^-$, the final redox-balance would be achieved by the reduction of I$_2$ either by SOF$_2$ or SO$_3^-$ which are stoichiometrically equivalent. In the case of Fe(CN)$_6^{4-}$, material balance requires that SOF$_2$ must be hydrolysed without a further increase in the oxidation state of the sulfur.

Unfortunately, in this system the final state of the sulfur could not be determined, however, SO$_3^-$ seems the most likely product.

These mechanistic considerations can be summarized by the following general reaction scheme:

\[
SF_6 + A^- \xrightarrow{hv} SF_5^- + A \quad [7]
\]
While this reaction sequence is consistent with the essential features observed in the radiation chemistry and photochemistry of aqueous solutions containing SF₆, the possibility of additional significant reactions exists. Indeed, the fact that F⁻ cannot always be considered as an inert product, places a limitation on the use of the relationship \( \xi(e^{-aq}) = \xi(F^-/6) \). However, the use of simple reagent blanks should provide a reasonable basis on which to assess the lability of F⁻ in a particular system.

The anomalous retention of N₂ in the photolysed Ru(CN)₆³⁻ - N₂O solutions containing SF₆ is an example of the departure from the simple mechanistic schemes which have thus far been presented for the reactions of N₂O and SF₆. It seems that somehow the presence of SF₆ in these solutions has transformed the 'predictably' inert N₂ molecule into a labile species. Admitting the evidence suggesting an N₂ fixation reaction

\[
(SF_6^- \rightarrow SF_5^- + F^-) \quad [5b]
\]

\[
SF_5^- + A^- \rightarrow SF_5^- + A \quad [6a]
\]

\[
(SF_5^- \rightarrow SF_4^- + F^-) \quad [6b]
\]

\[
SF_4^- + H_2O \rightarrow SOF_2^- + 2HF \quad [8]
\]

\[
SOF_2^- + 2H_2O \rightarrow SO_3^- + 2HF + 2H^+ \quad [9]
\]

\[
SO_3^- + 2A^- + H_2O \rightarrow SO_4^- + 2A^- + 2H^+ \quad [10]
\]
is inconclusive, the potential significance of such a reaction would seem to warrant proposing a speculative mechanism.

The suggestion of a species such as Ru(CN)$_5$N$_2$ would have little credibility were it not for the proven existence of Allen and Senoff's ion, Ru(NH$_3$)$_5$N$_2$'. Albeit there is little basis for comparing CN$^-$ and NH$_3$ as ligands, yet certain features in the synthesis of Ru(NH$_3$)$_5$N$_2$ suggest possible advantages with a cyano ligand system.

The common preparative route to Ru(NH$_3$)$_5$N$_2$ involves hydrolysis of the monohalogenopentaamine. The subsequent substitution of N$_2$ for H$_2$O would most probably involve the five coordinate pentaamine intermediate.

$$\text{Ru(NH}_3)_5 X^{+1} \rightleftharpoons \text{Ru(NH}_3)_5 \text{H}_2\text{O}^{+2}$$

$$\text{Ru(NH}_3)_5 \text{N}_2^{+2} \rightleftharpoons \text{N}_2^{-2} \{\text{Ru(NH}_3)_5\}^{+2}$$

Since neither Allen nor his co-worker have ventured to propose a mechanism, the simple scheme given above is not offered as a serious proposal. However, if the rate determining step is in fact the formation of the pentacoordinate Ru(II) intermediate, then the N$_2$ fixation reaction should be facilitated by an increased stability in the intermediate as would be the case with CN$^-$ ligands. It is noteworthy that the isovalent intermediate Co(CN)$_5$ is reported to have sufficient stability to act as a discriminating intermediate (i.e. it has a sufficient lifetime to discriminate between the solvent and other dissolved nucleophiles).
Thus, the species Ru(CN)$_5^{-3}$ may be a suitable intermediate for fixing N$_2$.

Several features require special comment. The amount of N$_2$ available in the photolysed solutions is extremely small (i.e. $\sim 5 \times 10^{-6}$ M) yet from the retarded N$_2$ evolution in the gas analysis procedure it appears that approximately 90% of the N$_2$ has been 'fixed'. This obviously requires an extremely efficient scavenger such as an intermediate of relatively high stability (Ru(CN)$_5^{-3}$ ?). The 'reaction' also requires the presence of SF$_6$ and since SF$_6$ is itself inert the important component must be one of its decomposition products. The most apparent product would be H$^+$ which will react with the CN$^-$ liberated by photohydrolysis. Thus, Ru(CN)$_5$H$_2$O$^{-3}$ would not be so susceptible to the normally rapid anation reaction. The photofixation reaction could be visualized as follows:

$$\text{Ru(CN)}_6^{-4} + h\nu(> 2537\text{Å}) \rightarrow \text{Ru(CN)}_5\text{H}_2\text{O}^{-3} + \text{CN}^-$$

$$\text{H}^+ + \text{CN}^- \rightleftharpoons \text{HCN}$$

$$\text{Ru(CN)}_5\text{H}_2\text{O}^{-3} \rightleftharpoons \text{Ru(CN)}_5^{-3} + \text{H}_2\text{O}$$

$$\text{Ru(CN)}_5^{-3} + \text{N}_2 \rightarrow \text{Ru(CN)}_5\text{N}_2^3.$$

The gradual evolution of N$_2$ from the photolysed solutions with successive freeze-thaw cycles might simply be the result of the decomposition of the complex by the thermal shock of the procedure.

While the novelty of these proposed reactions encourages additional work in this area two serious contrary observations must also be included. The addition of H$^+$ to a Ru(CN)$_6^{-4}$ solution did not produce
the same effect as with \( \text{Ru(CN)}_6^{-4} - \text{N}_2\text{O} - \text{SF}_6 \) creating doubt about the role of \( \text{H}^+ \). The second observation was the lack of any unique absorption bands in these solutions. \( \text{Ru(NH}_3)_5^+ \text{N}^2_2 \) is reported to have bands at 263 m\( \mu \) and 221\( \text{m} \mu \), however changes in both extinction coefficient and 10 Dq may account for the lack of observable bands for a species such as \( \text{Ru(CN)}_5^+ \text{N}^2_2^{-3} \).

While the possible formation of the novel compound \( \text{Ru(CN)}_5^+ \text{N}^2_2^{-3} \) would appear to be the most significant feature of the photochemistry of \( \text{Ru(CN)}_6^{-4} \), it should still be recalled that the principal product of the 2537\( \AA \) photolysis is \( \text{e}^{-}\text{aq} \) (i.e. \( \xi(\text{e}^{-}\text{aq}) = 0.37 \)). Since ruthenium and iron are congeners it seems reasonable that \( \text{Ru(CN)}_6^{-4} \) and \( \text{Fe(CN)}_6^{-4} \) would exhibit similar photochemical activity. In comparing these ions a certain degree of independence of the specific excited state can be assumed provided that the excitation processes are of the same type (i.e. CTML). Thus the qualitative similarities observed in the photochemistry of \( \text{Ru(CN)}_6^{-4} \) and \( \text{Fe(CN)}_6^{-4} \) are consistent with the overall similarities of these two compounds.

The decrease in \( \xi(\text{e}^{-}\text{aq}) \) in going down a group in the Periodic Table has a precedence in the halide series where \( \xi(\text{e}^{-}\text{aq}) = 0.34 \) with \( \text{Br}^- \) and \( \xi(\text{e}^{-}\text{aq}) = 0.23 \) with \( \text{l}^- \)\( (16) \). However, two points should be considered before this trend is compared with the \( \text{Fe(CN)}_6^{-4} \) and \( \text{Ru(CN)}_6^{-4} \): firstly, the excitation processes involved in the halide

* The \( \text{H}^+ \) generated by \( \text{SF}_6 \) provides a 'steady' supply of \( \text{H}^+ \) whereas by adding \( \text{H}^+ \) as \( \text{HClO}_4 \) at a low concentration the \( \text{H}^+ \) may be depleted too rapidly and at the high concentration it may interfere as a scavenger of \( \text{e}^{-}\text{aq} \).
series are not the same as those in the case of the hexacyanometallates (CTTS as opposed to CTML) and secondly, within the halide series different wavelengths have been used to ensure the same excited state for each ion. Thus, for instance, for I⁻ solutions illuminated with 2537Å light $\xi(e^{-aq}) = 0.23$ but with the same wavelength the yield is zero for Cl⁻ solutions ($\xi(e^{-aq}) = 0.43$ at 1849Å). Since only the 2537Å line was used with the Ru(CN)₆⁻⁴ and Fe(CN)₆⁻⁴ solutions and since no interpretation of the ultra-violet spectra Ru(CN)₆⁻⁴ is available it cannot be assumed that identical states for both ions have been excited.

The formation of e⁻aq from a precursor state produced by a CTML excitation was briefly discussed before (see page 8). It was noted that this type of excitation could be envisaged as leaving the ligand with an excess negative charge which the solvent could readily abstract. Since such a process would depend on the degree of localization of this excess charge on the ligand, it might reasonably be anticipated that increasing covalency (ligand-metal orbital mixing) would decrease the probability of such an electron transfer. Indeed, this is observed between Fe(CN)₆⁻⁴ and Ru(CN)₆⁻⁴ where the latter should naturally be the more covalent. Again, such an explanation may be irrelevant to the results obtained here if different excited states were involved. This latter point is exemplified by the Pd(CN)₄⁻² and Pt(CN)₄⁻². As in the previous case Pd and Pt are congeners and have relatively strong absorption bands in the region of 2537Å. However, from detailed studies of these ions Batiste assigned these bands in Pd(CN)₄⁻²
to ligand field transitions but in \( \text{Pt}(\text{CN})_{4}^{2-} \) as CTML. The reasonable expectation on irradiation with 2537 Å light of the respective aqueous solutions was photohydrolysis with \( \text{Pd}(\text{CN})_{4}^{2-} \) and \( e^{-} \text{aq} \) formation with \( \text{Pt}(\text{CN})_{4}^{2-} \). As documented earlier, both complexes appear photochemically inert at this wavelength.

The apparent inert character of these complexes is rather novel particularly since the analogous \( \text{PtCl}_{4}^{2-} \) is photohydrolysed efficiently by normal laboratory lighting (\( \text{Pd Cl}_{4}^{2-} \) undergoes rapid hydrolysis even in complete darkness). The tetracyano complexes of Pd and Pt are clearly much more covalent than the tetrachloro complexes and the lack of photochemical activity in these complexes may again reflect the effect of charge delocalization through strong ligand-metal orbital mixing. Overall, however, these negative results provide positive evidence of the fallibility of anticipating the photochemistry of a compound solely on the basis of a knowledge of its excited states.
References


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