MASTER

PHOTOCONDUCTIVITY STUDIES OF THE FERROCYANIDE ION UNDER HIGH PRESSURE

BY

MARTIN I. FINSTON

B.S., B.A., University of Rochester, 1973
M.S., University of Illinois, 1975

THESIS

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy in Physics
in the Graduate College of the
University of Illinois at Urbana-Champaign, 1979

Urbana, Illinois

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EB

To
my parents,
Harmon and Edythe Finston

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ION UNDER HIGH PRESSURE

Martin I. Finston, Ph.D.
Department of Physics
University of Illinois at Urbana-Champaign, 1979

A novel apparatus was developed for the investigation of photoconductivity phenomena in liquids pressurized up to 10 kbar. A variety of exciting light sources could be used. In nonpolar solvents, with an applied d.c. voltage, photocurrents as small as 10 p.a. could be resolved. In aqueous solutions, with an applied voltage oscillating at 1 khz, light-induced conductivity changes as small as 0.01% could be resolved.

The photoaquation of the ferrocyanide ion was studied using the high-pressure photoconductivity apparatus and a steady-state high-pressure mercury lamp. The first-order photocurrent rise-time could be related to the relative quantum efficiency of the photoaquation process, while the dark decay of the photocurrent yielded a relative value of the bimolecular rate-constant for the reverse reaction. Kinetic measurements were carried out on dilute solutions of potassium ferrocyanide in pure water, and in 20% ethanol.

The photocurrent yield in aqueous solution was dependent upon secondary chemical equilibria which were sensitive to pressure in a predictable way. In ethanolic solution, the dependence of photocurrent yield on pressure

followed the variation of the reciprocal solvent viscosity. In both aqueous and alcoholic solution, the photoaquation quantum efficiency decreased exponentially with pressure, as did the bimolecular rate-constant for the dark reaction in aqueous solution. The pressure dependence of the bimolecular rate-constant in the alcoholic solution indicated a diffusion-limited process.

The pressure dependence of the photoaquation quantum yield, and of the bimolecular rate-constant in aqueous solution, was interpreted in terms of an activation volume model. The photoaquation data for both the aqueous and the alcoholic solutions agreed with a hypothetical mechanism whereby ligand-to-metal bond-breaking, and solvent-to-metal bond-formation, are effectively simultaneous. The results for the aqueous dark reaction strongly indicated breaking of the solvent-to-metal bond as the rate-limiting step.

A concluding section discusses the wide range of photochemical and photophysical studies to which the photoconductivity apparatus described here, using high-power pulsed laser excitation, is ideally suited.

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1. INTRODUCTION

1.1 General Background

The photochemistry of the ferrocyanide ion has been studied for many years. It is of current interest to the biophysicist as a model compound, and to the solar technologist as a potential photovoltaic fuel.

Vogler and Kunkely [1] have written that the photochemical dissociation of the ferrocyanide ion, and of the closely related carbonylpentacyanoferrate ion, bear a close resemblance to the photodissociation of CO- and CN-hemoglobins, which are, like the simpler compounds, low-spin Fe(II) complexes. Theoretical calculations suggest that, as is known to be the case for ferrocyanide and carbonylpentacyanoferrate, so too in the case of the hemoglobins, the photochemical release of CO and CN⁻ occurs from low-lying ligand field excited states.

Besides the photoaquation reaction which is studied in this work, the ferrocyanide ion has long been known to undergo photooxidation at wavelengths less than 337 nm. The product of this reaction is the ferricyanide ion, plus a hydrated electron. As early as circa 1900, a photovoltaic cell was constructed which utilized this reaction [2]. More recently, this reaction was discussed as a prospect for large-scale solar energy conversion cells. The study of the (lower energy) photoaquation reaction is important in this context, because it is unknown whether the two reactions compete in the spectral range where both occur.

It is known that the quantum efficiency for hydrated electron production is as high as 0.89 at 214 and 228 nm, while it drops to undetectable levels for wavelengths greater than 337 nm. [3].

The object of this study is to find evidence for or against the various possible models for the mechanism of photoaquation of the ferrocyanide ion, and for the mechanism of the (thermally activated) reverse reaction. These ligand-exchange reactions fall under the general heading of Nucleophilic Substitution.

A nucleophilic substitution reaction is generally regarded as proceeding through the formation of an activated complex as the rate-determining step. The actual mechanism is usually interpreted in terms of two extreme mechanisms called, in the nomenclature of organic chemistry, "Substitution, Nucleophilic, Unimolecular (S_N1)" and "Substitution, Nucleophilic, Bimolecular (S_N2).". In the first of these, the activated complex is understood to have a coordination number which is less by one unit than that of the stable complex; in the second, it is greater by one. [4]

Langford and Gray [5] have objected to the S_N1 - S_N2 nomenclature on the grounds that the stoichiometry which is implicit here may be misleading in terms of the "intimate mechanism;" that is, the actual atomic and electronic rearrangements occurring in the formation of the activated complex. For

instance, suppose that an aquation reaction proceeds through the formation of an activated complex of augmented coordination number: the original ligands, as well as the incoming molecule of water, are coordinated to the intermediate species. Then the intimate mechanism is "bimolecular," but inasmuch as the solvent, whose concentration is effectively constant, is participating in the reaction as the "incoming ligand," the apparent molecularity of the reaction will be first order. Conversely, the activated complex for a ligand substitution may be of diminished coordination number, but if the incoming ligand is rapidly captured in a "solvent cage," the apparent molecularity may be second order.

These considerations have led Langford and Gray to reject the conventional nomenclature. Instead they classify ligand substitution mechanisms according to: 1) the effect on the rate constant of modifications in the entering and leaving groups; 2) the effect on the rate constant of modification of the electronic characteristics of ligands attached to the reacting site; 3) kinetic-isotope effects; and 4) solvent modifications. The last of these categories might be understood to include the variation of pressure, which is the experimental approach of this work.

In the classification scheme of Langford and Gray, which is adopted here, we distinguish between D (dissociative), A (associative), and I (interchange) mechanisms. If, in the

rate-determining step, the coordination number of the complex is augmented or diminished by one unit, we speak of an A or a D mechanism, respectively. I denotes any interchange of ligands between the inner and outer coordination spheres which occurs more rapidly than the reorganization of the outer coordination sphere; operationally, such a process must be regarded as occurring in a single concerted step.

The Interchange mechanisms are further subdivided, according to the experimental effects listed above. If the activation energy for the ligand substitution is affected by the assistance of the entering group, we speak of an I_a mechanism; if the activation energy is determined by the requirements of dissociation, we speak of an I_d mechanism. The associative and dissociative mechanisms are distinguished from the corresponding interchange mechanism by experimental kinetic data. The detection of an anticipatable kinetic effect of an extant (albeit short-lived) intermediate, which might, for example, react selectively, would be evidence for a D or A mechanism, rather than an interchange.

Historically, the study of ligand substitution reactions of transition metal complexes has concentrated on thermally activated reactions of the complexes of Co(III), Pt(II), and Cr(III). It has been possible to synthesize a great variety of compounds in these classes without great difficulty. The reactions of these compounds tend to be slow, lending themselves well to study by the classical techniques, including direct chemical analysis, photometry, and electrometry. [6]

In the case of Fe(II), there are few complexes with simple photochemistry; the approach to mechanistic study by variation in ligand properties is consequently ruled out. There remains the study of isotope and solvent effects as virtually the only key to the photochemical mechanism.

The use of direct chemical analysis in the study of the photoaquation of ferrocyanide encounters grave obstacles. The literature has many conflicting values for the quantum efficiency of photoaquation, determined by direct chemical analysis, because the reversibility of the reaction was not properly taken into account. [7]

Photometric measurements of reaction kinetics of ferrocyanide are limited in sensitivity by the low extinction coefficient of the ferrocyanide absorption bands, and by the fact that all ligand field absorption in this species is photochemically active. Furthermore, there is no fluorescence or phosphorescence from ferrocyanide or its photoproducts in aqueous solution at room temperature. [8]

It is evident that the study of the photochemical kinetics of ferrocyanide demands an in situ instrumental approach, and that an electrometric method is probably the best-suited. While the conductimetric method suffers from lack of specificity, its simplicity and high sensitivity make it the method of choice in a situation like the present one, where the photochemistry is simple, with a very small number of different product species. The conductimetric method does not

perturb the system under study, is compatible with a wide observational timescale, from tenths of a second to hours, and can easily be adapted to the design constraints of a high pressure cell.

In this project, pressure is used as a controllable parameter, which may be simply related to the mechanism for the ligand substitution reactions which are studied here. The activation energy for a substitution reaction couples to the pressure through the so-called "volume of activation," which is understood in terms of the Transition State Theory, and which serves as the basis for mechanistic arguments concerning the structure of the activated complex. With the great pressure range available for this project, even very small activation volumes can be measured.

By altering the composition of the solvent, we can vary the viscosity (and therefore, the mobility of ions) in an additional dimension to pressure alone, and so can separate simple diffusion effects from other effects.

1.2 History

A number of authors have reported the use of conductance measurements as an in situ technique for determining reaction kinetics at high pressure.

Baliga and Whalley [9] measured by a conductance technique, the first-order rate constant for the hydrolysis of methyl bromide and isopropyl bromide in aqueous solution at

pressures up to three kilobars. A pyrex cell was used, with platinum electrodes, and a liquid mercury piston, which communicated the pressure from the hydraulic liquid in which the conductivity cell was immersed. An a.c. bridge was the basis of the external circuitry for measuring resistance changes.

Hyne, et al [10], used a similar method for studying the rate of solvolysis of alkyl halides in ethanol-water mixtures as a function of pressure. In this work, the conductivity cell consisted of a pair of interconnected glass bulbs. Each bulb had a platinum bead electrode sealed into its wall, and a precision-bore side-tube containing a teflon piston for the transmission of pressure. External circuitry included an a.c. bridge. Pressures to four kilobars were attained in this apparatus, which was immersed in a hydraulic liquid.

Caldin, et al [11], used a high pressure temperature-jump apparatus to study conductimetrically, the rates of fast reactions in solution at pressures up to three kilobars. The cell for this work was made of perspex, with an end-cap of the same material, and sealed with a teflon piston. Stainless-steel electrodes were sealed through the cell-wall with epoxy cement. The cell was immersed in pressurized glycerol. The temperature-jump was provided by flash-heating with a laser beam directed through the transparent end-cap. Conductimetric detection employed an a.c. bridge; for fast measurements the bridge imbalance signal was converted to d.c., and displayed on an

oscilloscope. Conductance changes of 0.01%, with a time resolution of 0.1 ms, were measured by this means.

2. THEORY

2.1 The Crystal Field Theory of the Ferrocyanide Spectrum

It is a characteristic of the transition metals that the outermost ("n") shell has begun to fill before completion of the (n-1)d shell. The typical transition metal complex ion consists of a transition metal atom stripped of its n-shell electrons, and surrounded by 3-8 ligands in a fixed geometrical pattern. The Crystal Field Theory considers the splitting of the (n-1)d orbitals by the electrostatic field of the ligands, and uses the so-called Crystal Field Stabilization Energy which the system gains by preferential filling of the lower energy d levels, in order to explain the magnetic, optical, and chemical properties of transition metal complexes. A classic introduction to Crystal Field Theory is the book by C. Ballhausen. [12]

In the case of an octahedral complex, such as ferrocyanide, the five d-orbitals are split into two levels. The lower level includes the d_{xy} , d_{yz} , and d_{xz} orbitals; it is denoted t_{2g} . The upper level includes the orbitals $d_{x^2-y^2}$ and d_{z^2} ; it is denoted e_g . The coordinate system for this scheme places the six ligands at the corners of a regular octahedron centered at the origin, with every corner lying on one of the three coordinate axes. The d_{xy} , d_{yz} , and d_{xz} orbitals each have four lobes, with the region of maximum electron density oriented along the diagonals of the corresponding plane. The $d_{x^2-y^2}$

orbital has four lobes oriented along the x- and y-axes, while the d_{z^2} orbital has regions of maximum electron density oriented along the z-axis. As one would expect based on repulsion between the metal d-electrons and the ligands, the higher-energy orbitals are those which "point" directly toward the ligands. The ligand field splitting, denoted, for historical reasons, $10Dq$, is predicted by theory as

$$10Dq = \frac{5eqa^4}{3r^5} \quad (1)$$

when the ligands are treated as point charges q , and

$$10Dq = \frac{5e\mu a^4}{r^6} \quad (2)$$

when the ligands are treated as point dipoles μ . In these expressions, r represents the metal-to-ligand radius, and a^4 is the mean fourth power radius of the d electrons of the central ion.

The ferrocyanide ion consists of a ferrous ion coordinated by six cyanide ions. The ferrous ion contains six d-electrons in its outermost shell; because of the large ligand field splitting in this system, all six electrons occupy the t_{2g} level in violation of Hund's Rule. Consequently, the ferrocyanide ion is diamagnetic.

Molecular-orbital effects complicate the simple single band model given by Crystal Field Theory. In fact, the ligand

field region of the ferrocyanide absorption spectrum shows three bands. Two moderately weak bands due to spin-allowed ligand field transitions appear at 320 and at 270 nm, and a very weak spin-forbidden ligand field transition occurs at 422 nm. There is an intense absorption at 220 nm; this is a charge-transfer transition, believed by some authors to be metal-to-ligand in character, and by others to be a charge-transfer-to-solvent.

The ferrocyanide ion shows two interesting features in its photochemistry. For exciting radiation at wavelengths greater than 350 nm, the only photochemical reaction is photoaquation; ie, the exchange, upon irradiation, of one molecule of water for one cyanide ion in the inner coordination sphere. Other photosubstitution reactions which have been observed for ferrocyanide occur through secondary thermally-activated substitution reactions of the primary photoaquation product. For exciting radiation at wavelengths below 350 nm, there occurs the production of hydrated electrons.

The Crystal Field Theory has been used to predict the lability of transition metal complexes toward ligand substitution. The activated complex is assumed to be formed by either an associative or a dissociative step, and (assuming an initially octahedral complex) the geometry of the intermediate state of coordination number five or seven is stipulated to be that, from among the many possible choices, which maximizes the crystal field stabilization energy. By this argument, the

most likely intermediate geometry for a dissociative pathway is the regular square pyramid, while for the associative pathway, the most likely geometry is the octahedral wedge of coordination seven. The pentagonal bipyramid is the most favored structure in the intermediate case.

The loss of stabilization upon forming the activated complex is understood as a "crystal field activation energy" for the reaction. For the case of a strong-field octahedral d^6 complex, the crystal field activation energies (in Dq) for the square pyramid, pentagonal bipyramid, and octahedral wedge are calculated to be 4.00, 8.52, and 3.63, respectively. [6]

While the kinetic application of the Crystal Field Theory has been quite successful in predicting the lability of complexes based on the number of d electrons, it is clear that the crystal field energies are only a small part of the bonding energies in any real system. Consequently, this application finds real utility only in the discussion of differences of reaction rate among complexes which are identical in all respects but the number of d electrons.

One might perhaps extend the above argument to treat, qualitatively, at least, the difference in lability between the ferrocyanide ion in its ground, and ligand-field excited, states. It is clear that the electronic rearrangement due to a t_{2g} to e_g transition destabilizes the ground state nuclear configuration. The increase in electron density between ligand and metal will increase the repulsion along that axis,

lengthening and eventually promoting the breaking of, the metal-to-ligand bond. The depletion of electron density, in some directions, between the ligands will facilitate a nucleophilic attack on the central atom.

A good review of the theory of the ferrocyanide spectrum, and of the photochemistry of the ferrocyanide ion, is to be found in the book by Balzani and Carassiti [8]. Basolo and Pearson [6] discuss the kinetic application of the Crystal Field Theory.

2.2 The Transition State Theory and Volume of Activation

In the Transition State Theory for a simple chemical reaction, the rate constant, k , is understood to be determined by the equilibrium between the reactants, and a hypothetical "activated complex." The region of configuration space in which the activated complex is supposed to exist is referred to as the "transition state"; it is the neighborhood of a saddle point, where the energy maximum occurs along the reaction coordinate. The rate constant is given as

$$k = \frac{k_B T}{h} \exp (-\Delta G^\ddagger / RT) \quad (3)$$

This expression is frequently multiplied by a constant on the order of unity known as the "transmission coefficient"; i.e., the probability that the activated complex will dissociate into products instead of back into reactants. $\Delta G^\ddagger$ is the Gibbs Free Energy of Activation.

From thermodynamics, we know that $dG = VdP - SdT$.

Applying this to the expression for k , we have

$$RT(d/dP)_T \ln k = -(d/dP)_T \Delta G^\ddagger = -\Delta V^\ddagger \quad (4)$$

The quantity $\Delta V^\ddagger$ is known as the "Volume of Activation" of the chemical reaction.

A naive application of Le Chatelier's Principle might suggest that any reaction which is accompanied by a net contraction is accelerated by pressure. In fact, this is true only when the density in the transition state is intermediate between that in the initial and final states. Furthermore, since the activated complex is short-lived, and exists only in very minute concentration, the volume of activation is not accessible to ordinary dilatometric measurements.

No strictly theoretical analytical function exists which expresses the dependence of the rate constant k on pressure. The frequent assumption that $\ln k$ is linear in the pressure (i.e., that $\Delta V^\ddagger$ is independent of pressure) has not proven to hold, in general, over pressure ranges greater than 100 atmospheres. Other empirical functions which have been proposed are:

$$\ln k = A + BP + CP^2$$

and

$$\ln k = A + BP + CP^{1.523}$$

The second of these has been derived from the empirical Tait Equation.

The activation volume is regarded as the sum of two terms; one term is due directly to the changing interaction of the reacting molecules with one another when forming the activated complex, while the other includes all solvent effects on the volume:

$$\Delta V^\ddagger = \Delta V_R^\ddagger + \Delta V_S^\ddagger \quad (5)$$

$\Delta V_R^\ddagger$ is essentially the change in the net van der Waals volume when the activated complex is formed. The main contributions to this effect come from changes in bond length, and from changes in non-bonded interaction within the same molecule. An example of the latter would be the rearrangement of ligands, or of electronic orbitals.

Bond formation or contraction during the activation process would result in a negative contribution to $\Delta V_R^\ddagger$; bond stretching would result in a positive contribution.

Since the volume of mixing for non-hydrogen-bonding liquids is usually less than 1 or 2 cc/mole, it seems likely that in the absence of hydrogen bonding effects and charge-separation effects, that part of $\Delta V_S^\ddagger$ arising from the difference in solvent interaction between the reactants and the activated complex should be small.

When the activation involves separation of charge, there is a large contribution to $\Delta V_S^\ddagger$ due to electrostriction of the

solvent; indeed, this effect may be dominant in the determination of the sign and magnitude of $\Delta V^\ddagger$. Hamann [13] has calculated the decrease in solvent volume accompanying the formation of a full electronic charge on a small spherical molecule to be 10-30 cc/mole in most solvents; Couture and Laidler [14] have found a value of 26 cc/mole when the solvent is water.

Whalley [15] has presented a crude model for the electrostatic effect due to the molecular charge, and multipole moments: Assume that the molecule would occupy a spherical cavity of radius a_0 , in a medium of unit dielectric constant. Assume that the electric field of the molecule may be adequately represented by the sum of a point charge ze , dipole μ , and quadrupole Q , at the center of the cavity. The molecule is now embedded in an incompressible continuous dielectric medium ϵ ; the cavity remains spherical, with dielectric constant equal to unity inside the cavity. Under these assumptions, the change in Gibbs Free Energy when a molecule is transferred from the vacuum to the dielectric medium ϵ , is given by:

$$\begin{aligned} \Delta G_{es} = & -\frac{1}{2}N \frac{z^2 e^2}{a_0} \frac{\epsilon - 1}{\epsilon} - N \frac{\mu^2}{a_0^3} \frac{\epsilon - 1}{2\epsilon + 1} \\ & - \frac{3}{2}N \frac{Q^2}{a_0^5} \frac{\epsilon - 1}{3\epsilon + 2} \end{aligned} \quad (6)$$

It is evident, upon differentiating this expression with respect to pressure (with temperature held constant) that ΔV_{es} contains terms in $d\epsilon^{-1}/dP$, and in $d(\ln a)/dP$. The "dielectric term", $[d(\ln a)/dP]_T$, is usually, but not necessarily, negative in sign, while the "cavity" term is necessarily less than or equal to zero.

Using "typical" values, Whalley has made estimates of the value of $-\Delta V_{es}$ when the solvent is water:

	Dielectric	Cavity
Charge	1.3	12
Dipole 10D	1.8	17
Quadrupole 0.2×10^{-24} e.s.u.	1.4	13

Evidently, this theory predicts the compression of the cavity to be the dominant effect, given values roughly consistent with those of other authors, and predicts the same order of magnitude for "typical" monopole, dipole, and quadrupole effects.

In principle, arguments based on the volume of activation may permit one to employ pressure studies in order to distinguish between associative and dissociative mechanisms for solvolytic reactions. This method is especially powerful when the problem is to distinguish between mechanisms where charge is aggregated, on the one hand, and dispersed, on the other.

To date, the success of high-pressure studies of reaction kinetics in solution has been in the qualitative rationalization of activation volumes and mechanisms.

Reference [6] includes a discussion of the application of Transition State Theory to substitution reactions of octahedral complexes. General discussions and literature reviews of the activation volume method are found in References [16-17]. Reference [18] discusses the application of the Transition State Theory and the activation volume method to reactions of coordination compounds.

2.3 Conductimetry of Ionic Reactions

A chemical reaction which results in a net change in ionic conductance can be detected conductimetrically. A pair of electrodes is immersed in the sample solution, and the electrodes are connected, externally, to an oscillating voltage source, and to a device (e.g., an a.c. bridge) which is sensitive to changes in the alternating current between the electrodes. The applied voltage is usually in the range of one to ten kilohertz, for in this range, the current is carried almost exclusively by ionic migration, and in the complete absence of faradaic processes.

The conductimetric technique has the advantage of high sensitivity, and it can be used in situ without altering the properties of the sample. The disadvantages are the absence of selectivity, and the susceptibility to error induced by temperature fluctuations.

The specific conductance κ of a solution is the value obtained experimentally with a standard conductivity cell. The molar conductance Λ of an electrolyte at given concentration c is the ratio of specific conductance to concentration:

$$\Lambda = \kappa / c \quad (7)$$

At infinite dilution, the molar conductance of an electrolyte may be expressed as the sum of the molar ionic conductances of the component ions:

$$\Lambda_{\infty} = \lambda_{+}^{\infty} + \lambda_{-}^{\infty} \quad (8)$$

The values λ^{∞} are tabulated for many ions.

Let us now consider a simple, one-step reaction in which at least some of the reactants and products are electrically charged:

The r_i and p_j are the stoichiometric coefficients for the reaction. Assuming there is only one reaction, then it must be true that:

$$-r_i \frac{d}{dt}[R_i] = p_j \frac{d}{dt}[P_j] \quad (10)$$

for all pairs of indices (i, j) . This well-defined quantity is called the rate of reaction. Inasmuch as the rate of reaction is usually time-dependent, we denote it $v(t)$. For concentrations

of less than 10^{-3} molar, the assumption of infinite dilution properties is usually a good approximation. Introducing that assumption here, we then have:

$$\kappa = \sum_{i,j=1}^2 \lambda_i^0 [R_i] + \lambda_j^0 [P_j] \quad (11)$$

If the system is not in a stationary state, we have:

$$\begin{aligned} \frac{d\kappa}{dt} &= \sum_{i,j=1}^2 \left[\lambda_j^0 \frac{v(t)}{p_j} - \lambda_i^0 \frac{v(t)}{r_i} \right] \\ &= v(t) \sum_{i,j=1}^2 \left[\frac{\lambda_j^0}{p_j} - \frac{\lambda_i^0}{r_i} \right] \end{aligned} \quad (12)$$

Thus, the rate of reaction is proportional to the time rate of change of the specific conductance of the sample.

A good general discussion of conductance measurements may be found in Reference [19].

2.4 The Photochemical Cell

The purpose of this project is to determine the effect of pressure on the first-order rate-constant for aquation of the optically excited ferrocyanide ion, and to interpret the result in mechanistic terms. The optically excited ferrocyanide ion is not accessible to direct instrumental detection; therefore, the microscopic rate-constant will be deduced, indirectly, from quantum yield data.

Suppose that an optically excited molecule can be deactivated by any one of n different processes, which are all first-order, or pseudo-first-order. These may be either physical deactivation processes, such as vibrational or radiative relaxation, or they may be chemical reactions. If each deactivation process has first-order rate-constant k_n , then the actual lifetime τ of the excited state is given by

$$\tau = \left[\sum_n k_n \right]^{-1} \quad (13)$$

and, furthermore, the quantum yield ϕ_a for the "a"th process is given by

$$\phi_a = k_a \tau \quad (14)$$

Our object is to determine the value of $(d/dP)_T k_a$ for the aquation process.

In aqueous solution at room temperature, vibrational relaxation is the dominant physical relaxation process. In the pressure range considered here, namely, from one atmosphere to ten kilobars, the rate of vibrational deactivation does not change significantly.

It is known that for the excited state considered here, there is only one chemical deactivation process; namely, aquation. Thus, we can write

$$\phi_a = \frac{k_a}{\sum_{n \neq a} k_n^{\text{physical}} + k_a} \quad (15)$$

Furthermore, if $\phi_a \ll 1$, then the denominator is roughly independent of pressure, and thus

$$\ln k_a = \ln \phi_a - \ln \left(\sum_n k_n \right) \quad (16)$$

$$(d/dP)_T (\ln k_a) \approx (d/dP)_T \ln \phi_a$$

Evidently, it is sufficient to measure relative values for ϕ_a .

The relative quantum yield is evaluated from the macroscopic pseudo-first-order kinetics. Assume a cell of length l (cm), window area S (cm²), and volume V (cc). The cell is filled with a transparent medium containing a concentration c (moles/liter) of light-absorbing solute. Let I_0 denote the incident flux of monochromatic light (einstein/cm²-sec), and let I denote the flux of transmitted light. Then by the Lambert-Beer Law,

$$\log(I_0/I) = \epsilon_M c l \quad (17)$$

where ϵ_M is a property of the solute, known as the molar absorptivity (liter/mole-cm).

Let us denote by I_m the average number of einsteins absorbed in unit volume and unit time. Then

$$I_m = I_0 (S/V) (1 - 10^{-\epsilon_M c l}) \quad (18)$$

If ϵ_{M}^{cl} is much less than unity, we can approximate with

$$I_m \approx I_O (S/V) (2.303) \epsilon_{M}^{cl} \quad (19)$$

If the absorbing species undergoes a single, unimolecular photochemical reaction with quantum efficiency ϕ_a , then

$$-\frac{dc}{dt} = \phi_a I_m \quad (20)$$

$$= c (2.303 \phi_a I_O \epsilon_M^{cl} S/V)$$

We have derived a first-order rate law. The time constant, which can be measured, provides a value for the relative quantum yield [8].

3. EXPERIMENTAL

3.1 Apparatus

The purpose of the experimental apparatus is to illuminate a pressurized liquid sample with a narrow spectral range of ultraviolet light, and to measure small changes so induced in an alternating electric current passing through the sample. It must be possible to follow the signal accurately over time intervals ranging from several seconds to tens of minutes. Changes as small as 0.01 percent must be detectable in a background whose amplitude is typically about 300 microamperes. To accomplish the current measurement, a differential amplifier is employed. This component subtracts a synchronous, independently adjustable offset voltage from the IR-drop of the background current through a measuring resistor. Phase-locked amplification is used to amplify the difference-signal. While similar measurements usually employ an a.c. bridge the offset method used here has several advantages. The instrument response is necessarily always linear, and the output is a direct measure of the photocurrent. In addition, the method is conceptually simple, and it uses instruments which were readily available in the laboratory. For mechanical simplicity, and in order to use the pressure vessel as part of the electrostatic shielding, the sample cell was designed to have one electrode grounded through the pressure vessel. The sample is one component in a simple series circuit which also includes a voltage source,

and a current-measuring resistor. The voltage drop across the measuring resistor is the signal; it is input to the lock-in amplifier as a signal relative to ground. Thus, the ground-point in the circuit must lie between the sample and the measuring resistor. The consequence of this is that the voltage source in this circuit must have a floating output. This is accomplished through the use of an isolation transformer on the input to a battery-operated power amplifier. The independently adjusted offset signal is fed directly into the inverting input of the lock-in amplifier, and is referred to ground in the usual way. The measuring system is illustrated schematically in Figure (1).

The high pressure liquid cell used in this work is a modification of that described by Okamoto [20]. The cell is a cylinder made of Vascomax steel, hollow, with steel plugs at each end.

The window plug admits light to the cell through a cylindrical sapphire, whose c-axis is oriented perpendicular to the face of the cylinder. The sapphire is placed over the smooth, lapped surface of the window plug, with a brass cap attached over the inward face of the sapphire in order to prevent jarring. The pressure cell and window plug are shown in Figure (2).

The conductivity plug has the same dimensions as the window plug. A single electrical feedthrough is made in this plug by seating a stainless-steel cone in a pyrophyllite sleeve, which itself occupies a cone-shaped hole through the plug. The stainless-steel cone tapers from the inside toward the outside.

Figure 1. Block diagram of high pressure liquid photoconductivity apparatus.

Figure 2. The outer high pressure cell, including window plug and detail of the seal. The sapphire window is not shown.

The outer end of the cone, where it comes to a point, is soldered to a copper wire. This wire is soldered, at its other end, to a microphone jack, which is firmly held, by a set-screw, in a cylindrical cavity in the outer end of the electrical plug. The electrical plug is shown in Figure (3).

The high pressure seals for this cell work by Bridgman's principle of unsupported area. This principle states that if the seal area on the high pressure side exceeds the area on the support side, then the pressurized fluid will not leak past the region of the seal. The seal consists of three rings: a stainless steel backup ring, a brass ring, and a ring of leaded steel. The backup ring is employed to prevent the other rings from jamming in the cell. The brass ring forms the seal at lower pressures, while the leaded steel ring, which, by virtue of its greater hardness, suffers less compression than the brass ring, forms the seal at the highest pressures used. The dimensions of the leaded steel ring are such that it does not touch the sides of the plug at atmospheric pressure.

The inner cell contains the sample solution. In order to provide electrical isolation and chemical inertness, the inner cell is made from nylon. Light is admitted to the inner cell through a sapphire window, which is sealed into one end with epoxy cement. Pressure is transmitted to the contents of the inner cell by means of a nylon piston, which is sealed into the end opposite the window with a Teflon O-ring. Electrical

HIGH PRESSURE PLUG FOR CONDUCTIVITY

Figure 3. Detail of the high pressure conductivity plug. The inner cell screws onto the brass holder at lower right.

contact with the sample solution is made through platinum foil electrodes. These electrodes are fastened, with epoxy cement, to the inner faces of threaded bakelite plugs. A minute drop of solder is used to attach a fine copper wire to each electrode. The wire is insulated with vinyl, and the soldered joint is made as close as possible to the insulation in order to provide mechanical reinforcement. The wire is drawn out through a tight hole which is bored entirely through the center of the plug. The inner cell is shown in Figure (4).

A brass key is used to align the electrode plugs. The key is inserted, and then the plugs are screwed into the sides of the inner cell and tightened up against the key. Tightening of the plugs is facilitated by shallow holes drilled into the outer face of the plugs, at opposite sides. The pointed tips of a pair of curved forceps are inserted into the holes, and the forceps can be used as a wrench. After the plugs are tightened against the insert, they are loosened one-half turn, the insert is withdrawn, and the plugs are tightened again. At this point, the outer face of each plug is not flush with the nylon cell, but, rather, is recessed into it. The plug is painted over with epoxy cement, and, after the first layer is hardened, a second layer is applied while the inside of the cell is attached to a vacuum line. The vacuum is maintained while the second layer of cement hardens. The final seal is made with a solution of uncured epoxy cement in diethyl ether. With vacuum applied to the inside of the cell, the outside is

PHOTOCONDUCTIVITY INNER CELL

Figure 4. The photoconductivity inner cell.

painted with the ether solution. The ether penetrates remaining cracks and pores in the seal, filling them up with residual epoxy cement as it evaporates.

Because the inner cell is subject to compression under high pressure, the epoxy seals crack. In order to prevent leaking, a new application of the epoxy-ether mixture is required after every pressure run. After, typically, every third run the window is pushed out and the old epoxy window seal is replaced. After, typically, every sixth run, the lead wires have become too short, from repeated soldering, snipping, and desoldering, for further use. When this point is reached, the old bakelite plugs are drilled out and replaced.

The inner cell has a threaded base by which it screws onto a perforated brass holder. The brass holder screws onto the inner end of the conductivity plug. The leadwire from one bakelite electrode plug makes contact to the wide (inner) end of the stainless steel cone of the electrical feedthrough; the leadwire from the other electrode plug is attached to a brass screw which fastens to the body of the plug for grounding.

The pressurizing fluid is hexane. Pressurization is accomplished using an intensifier; transmission to the cell is through a high pressure line. The intensifier uses hydraulic pumps to apply pressure against a four-inch piston. This piston drives a three-fourths inch piston which is forced against the hexane. For experiments requiring accurate pressure

data below 2.5 kilobars, a 50,000 psi gauge is used to monitor the hexane pressure directly. For work at higher pressures the applied hydraulic pressure is read from a Heise Bourdon gauge, and the hexane pressure is obtained from a calibration curve of hexane pressure vs applied pressure. The calibration curve is checked regularly with a manganin gauge. Details of the intensifier pressure seals and design are given by Okamoto.

The light source is an Osram 200-watt Super Pressure mercury lamp tube, in a Schoeffel LH150 lamp housing, and powered by a Schoeffel LPS271 lamp power supply. Spectral isolation is accomplished with a Jarrell-Ash 82-410 quarter meter Ebert monochromator. The grating used in this project is blazed at 3000 Angstroms; and has a linear dispersion of 33 Angstroms per millimeter. An exit slit of width 6 millimeters was used, providing a 20 nanometer wide output band, centered on the 365 nanometer emission line of mercury. This combination was chosen in order to maximize the light output in the broad ligand field absorption region of the sample while minimizing the output to the charge transfer band, which lies further in the ultraviolet, and to the absorption band, which lies further in toward the visible.

A master oscillator provides a one kilohertz reference signal for the oscilloscope triggers, the lock-in amplifier, and the floating power supply-offset device. The oscillator is built around an Intersil 8038 Waveform Generator integrated circuit. The floating power supply-offset device was designed

in collaboration with Carl Reiner of the Electronic Engineering Services office of the Chemistry Department. This device has a single input; namely, the reference signal from the master oscillator. The "phase output" provides the offset signal, referred to ground. The amplitude and phase of this signal can be adjusted by manual knobs. This signal is connected to channel "B" of the lock-in amplifier. The "load output" is produced between a pair of isolated terminals, since it is a floating signal. This is the power input to the sample (load). One terminal goes directly to the electrical feedthrough of the pressure cell. The other terminal connects to ground through the measuring resistor. The output amplitude can be adjusted with a manual knob.

The measuring resistance is provided by a decade box; the IR drop across it is connected to input "A" of the lock-in amplifier. A resistance of 300 Ohms was ordinarily used in connection with the aqueous samples, and a resistance of 900 Ohms with the alcoholic samples.

The lock-in amplifier was a PAR Model HR-8, with a PAR Type D differential input preamplifier. The instrument settings were $Q=10$, filter time constant = 300 ms, rolloff = 12 db/octave. The recorded output of the lock-in amplifier was connected to a Houston Instrument Omniscrite strip-chart recorder.

Two oscilloscopes were used. The voltage across the sample was monitored with a Data Instruments Model 555

oscilloscope. The two inputs to the lock-in amplifier were displayed on a Tektronix Type 545 oscilloscope with Type CA plug-in unit (dual trace calibrated preamplifier).

A detailed schematic diagram of the power supply and offset circuits is given in Figure (5).

Figure 5. The power supply and offset circuit. Master oscillator is at top, floating amplifier in middle of diagram, and phase shifter-offset amplifier at bottom.

3.2 Procedure

3.2.1 Preparation of Samples

The potassium ferrocyanide used was Baker Reagent Grade, without further purification.

The aqueous solutions were prepared as follows: 20 milligrams of potassium ferrocyanide were weighed out, and added to a 250 milliliter amber-colored Ehrlenmeyer flask. 200 milliliters of deionized, distilled water were added to the flask, and the contents were stirred until dissolution was complete. The solution was purged by bubbling with argon in a dark room for 15 minutes.

Two different methods were employed for the preparation of the alcoholic solutions. The method of preparation made no difference in the experimental results.

In the first method, 18 milligrams of potassium ferrocyanide were added to the 250 milliliter amber flask. 100 milliliters of deionized, distilled water were added, with stirring. After complete dissolution of the salt, 80 milliliters of absolute ethanol were dripped slowly into the flask from a buret; during this step, stirring and gentle heating were maintained. The solution was allowed to cool to room temperature, and then purged for 15 minutes with ethanol-saturated argon.

In the second method, 18 milligrams of potassium ferrocyanide were added to a 25 milliliter Ehrlenmeyer flask. Separately, to the 250 milliliter amber flask were added 80

milliliters of deionized, distilled water, and 80 milliliters of absolute ethanol. 20 milliliters of deionized, distilled water were added to the 25 milliliter flask, and stirred until the potassium ferrocyanide was completely dissolved. With constant stirring of the amber flask, the potassium ferrocyanide solution was transferred, drop-by-drop, to the alcohol-water mixture, with a Pasteur pipette. The contents of the amber flask were then purged for 15 minutes with ethanol-saturated argon.

All sample solutions were carefully protected from ultraviolet light at all times.

The loading of the inner cell was performed inside a glove bag, which had previously been purged with argon for 15 minutes. Prior to insertion into the glove bag, the Teflon O-ring was pushed onto the nylon piston of the inner cell. Inside the glove bag, the sample was transferred from the 250 milliliter amber flask to the inner cell by means of a Pasteur pipet. The pipet was then used to remove bubbles from the recesses of the cell. After removal of bubbles, the cell was filled to overflowing with an extra charge of solution from the pipet, which had been carefully cleared of bubbles. The piston was then immediately pushed in until it was firmly set, and liquid was expelled from the cell. The outside of the cell was then dried with Kimwipes, and the cell removed from the glove bag. A new batch of sample solution was made up for each such load.

3.2.2 Loading the Conductivity Plug

Prior to loading, the lead-wires of the conductivity plug are replaced, if necessary. The brass holder is then screwed on, and the lead-wires are drawn out through opposite perforations in the holder. The nylon inner cell, which has been filled with the sample solution, is screwed onto the end of the brass holder. Before connecting the leads from the inner cell with those from the conductivity plug, the ends are freshly tinned. The ends are then crossed at their centers, and a straight joint is made by winding the outer half of each end about the inner half of its partner. The splice is completed by application of the hot tip of a soldering iron. In order to provide insulation and mechanical reinforcement, the joint is tightly wrapped in Teflon dope tape. The lead-wires are tucked inside the brass holder, underneath the piston of the inner cell. On each side, a short length of wire protrudes from inside the brass holder, in order to connect with the electrode plug of the inner cell. This section of wire sits flush in a groove cut in the outside of the brass holder, and in the lower half of the nylon cell. A strip of Teflon tape is wrapped tightly around the brass holder, at the level of the grooves, in order to hold the wires in place. The inner cell is then wrapped in aluminum foil to guard against accidental irradiation until it is loaded into the outer high-pressure cell.

3.2.3 Loading the Outer Cell

The first step in loading the outer cell is to assemble the window plug and its seal. The window plug is then torqued to 1200 inch-pounds in order to set the seal. The seal for the conductivity plug is then assembled, and the pressure cell filled with spectrophotometric grade hexane. Air bubbles are removed from the hexane by vigorous agitation of the cell. The aluminum foil shield is then removed from the nylon inner cell, and the conductivity plug screwed in until finger-tight. Continuity of the electrical circuit is then tested with a Simpson multimeter on the RX100 and RX10,000 scales. The conductivity plug is then torqued to 1200 inch-pounds, and the electrical circuit is tested again. All experimental measurements were performed at ambient room temperature.

3.2.4 Adjustment of the External Circuit

The first step of the start-up procedure is to switch on the master oscillator (with output gain at minimum setting), switch on the floating amplifier-phase shifter (with "load" gain at the minimum setting), and switch on the lock-in amplifier. The output gain of the master oscillator is then adjusted to provide an adequate reference signal for the lock-in amplifier. The "load" output is then plugged into the pressure cell, and, using the single-trace oscilloscope as a monitor, the master oscillator output gain, and the "load gain," are adjusted to provide the desired voltage amplitude

across the sample. Precise adjustment of the frequency of the master oscillator is then made.

At the beginning of the signal optimization procedure, the lock-in amplifier is set to its least sensitive range. Using the dual-trace oscilloscope as a monitor, the amplitude and phase of the offset signal are set to approximately match the waveform of the voltage across the measuring resistor. The lock-in amplifier is tuned in on channel A (measuring resistor). The channel selector on the lock-in is then switched to "B," and the phase of the offset signal is finely adjusted to give the maximum reading. The channel selector is then switched to "A-B," and the amplitude of the offset signal is finely adjusted to give a zero signal. This last procedure is performed stepwise, at successively greater values of the gain of the lock-in amplifier, until the operating sensitivity is reached. The strip-chart recorder is then turned on, and the null position of the recorder pen is adjusted with both the offset knob of the recorder, and the offset control of the lock-in amplifier.

3.2.5 The Measurement Procedure

The first step in performing a measurement is to set the initial pen position, and to turn on the recorder chart drive. The sample is illuminated by manually raising the shutter. Exposure is continued for a duration of about one time-constant. The shutter is then manually closed, and recording is continued until the signal comes within ten percent

of its dark steady-state level. The recorder pen is then lifted, and the recorder shut off.

In order to avoid exhaustion of the sample, each load is subjected to only three exposures. These exposures are made at three different values of the applied pressure, usually with a spacing of one kilobar between successive measurements. The total pressure range for each run is so chosen as to provide considerable overlap among the various runs. The phase and amplitude of the offset signal are adjusted before making the measurements at each new pressure.

3.2.6 Data Analysis

The experimental curves are digitized, and stored on magnetic disk. The spacing of digitized points is typically twenty-five points per time constant. A non-linear least squares curve-fitting program is used to fit the data points to an analytical curve. The analytical curve for the unimolecular kinetics has the form

$$y = p_1 + p_2 \exp(-p_3 t) \quad (21)$$

while the analytical curve for bimolecular kinetics has the form

$$y = p_1 + p_2 / (1 + p_3 t) \quad (22)$$

In almost all cases, an excellent fit was obtained.

The unimolecular decay constant, k_1 , was obtained directly, from

$$k_1 = p_3 \quad (23)$$

The interpretation of the data for the bimolecular decay constant is more involved since, where k_1 is independent of all units except time, and is therefore independent of the measuring system, the dimensions of k_2 are l/mole-sec, which can be related to the temporal characteristics of the signal voltage only through knowledge of the overall gain of the measurement system, in (moles of reaction)/volt. Unfortunately, this factor will undergo modest variation with the application of pressure. Examination of the amplitude of the photocurrent curves enables us to estimate the changes in the overall gain.

The bimolecular reaction has the form

with the concentration of A necessarily equal to the concentration of B. Let the instantaneous concentration of A be denoted n ; then the signal voltage $V(t)$ will be related to n through the overall gain, G , defined above:

$$V(t) = Gn(t) \quad (25)$$

Now the rate of change of n obeys

$$(d/dt)n = -k_2 n^2 \quad (26)$$

which is integrated to yield

$$n = n_0 / (1 + n_0 k_2 t) \quad (27)$$

From comparison with the analytical curve of the computer-fit, Equation (22), it is evident that p_2 is identical with Gn_0 , and p_3 is identical with $n_0 k_2$. The value of k_1 is an artifact, and cannot be invoked in the data analysis. Clearly, k_2 can only be evaluated to within a factor of G , which will depend upon pressure at least by the effect of pressure on ionic mobility.

Since concentrations of reactants are changed by compression of the solvent, the measured value of k_2 must be corrected for this effect. Let us denote by w the relative volume of the solvent; w is defined as unity at one atmosphere. Now at one atmosphere, we have

$$(d/dt)n = -k_2^{1 \text{ atm}} n^2 \quad (28)$$

and at any arbitrary pressure,

$$(d/dt)n = -k_2^P n^2 \quad (29)$$

Now we denote by $k_2^O(P)$ the compression-corrected bimolecular rate-constant; it is defined by

$$(d/dt)(n/w) = -k_2^O(P) (n/w)^2 \quad (30)$$

By comparison of the last two equations, we find that

$$k_2^O(P) = w k_2^P \quad (31)$$

i.e., the correction for compression of the solvent is accomplished by multiplying the apparent rate constant at a given pressure by the relative solvent volume at that pressure.

The purpose of the kinetic measurements of the (first-order) photochemical reaction is to determine the variation with pressure of the microscopic rate-constant for aquation of the optically excited state. This is not measured directly, but is deduced from the variation of the quantum yield. For infinitesimal quantum yield, the microscopic rate constant and the quantum yield are proportional to each other. For finite quantum yield, a correction to the primary data is necessary [see Figure (6)].

From Equation (15),

$$\phi = k^{\text{chemical}} / (k^{\text{chemical}} + \sum_i k_i^{\text{physical}}) \quad (32)$$

whence

$$k^{\text{chemical}} = \left(\frac{\phi}{1 - \phi} \right) \sum_i k_i^{\text{physical}} \quad (33)$$

In this work, $\sum_i k_i^{\text{physical}}$ is assumed to be essentially independent of pressure, and is treated as a multiplicative constant. The currently accepted one-atmosphere value of ϕ for the photoaquation of ferrocyanide at the wavelength and range of pH used in this work is 0.2 [3,7]. At the highest pressures

Figure 6. The relationship between quantum yield for photoaquation (ϕ) and microscopic first-order rate constant k_1 in the aqueous ferrocyanide system under pressure.

used in this work, the value of the quantum efficiency is small enough to justify the linear approximation. At atmospheric pressure, a correction of 20% is necessary in order to get k^{chemical} from the relative value of ϕ .

4. RESULTS

In order to determine the effect of solvent composition on the photocurrent yield and kinetic parameters, experimental measurements were performed at one atmosphere using fresh solutions containing, respectively, 0, 20, and 30 mole-percent ethanol. The sign of the photocurrent was observed to reverse, in going from the pure aqueous solvent to 20-percent ethanol. A solvent composition of 10-percent ethanol gave an extremely small value of the photocurrent, suggesting that the zero-crossing occurs near that composition. The results of the one-atmosphere measurements are shown in Table (1). The relative change induced in the bimolecular recombination constant by changing the solvent composition may be estimated by taking the ratio of the limiting photoconductivity amplitude to the recombination half-life as a relative measure of the bimolecular rate-constant.

The dependence on pressure of the limiting photocurrent in both aqueous and ethanolic solutions is shown in Figure (7). The aqueous data and the ethanolic data have been normalized relative to each other in this figure so as to facilitate visual comparison. In order to make absolute comparisons of the two sets of data, it is necessary to refer to the one-atmosphere values of the limiting photoconductivity amplitude tabulated in Table (1). Curves representing the inverse viscosity as a function of pressure for twenty-percent ethanol at room

Table 1. Table of atmospheric pressure numerical data

Mole - % Ethanol	Photocurrent Rise Time (Min)	Recombination Half-Life (Min)	Limiting Photoconductivity Amplitude (μ)
0	1.3	1.0	-1.3
20	0.7	0.8	0.1
30	0.8	0.7	0.2

NOTE: All solutions are 2.4×10^{-4} M.

Applied voltage for these measurements was 0.1 Volt (peak-to-peak)
at 1 kHz.

Figure 7. The pre-exponential factor in aqueous (lower curve) and 20% ethanolic (upper curve) solution. The viscosity data for water are from Bridgman [22].

temperature, and for water at zero Celsius degrees, are superposed on the data in Figure (7). The ethanolic data show good agreement with the inverse viscosity curve throughout the experimental range of pressure. The aqueous data approach the inverse viscosity curve at the highest experimental pressures.

The dependence of the photochemical quantum efficiency on pressure for the aqueous solutions is shown in Figure (8). A straight-line fit was drawn by eye, yielding a value of 6.15 cc/mole for the activation volume.

The dependence on pressure of the bimolecular recombination constant in aqueous solution is shown in Figure (9). In addition to the raw data, corrected data points are included in Figure (9), which take into account the variation with pressure of the overall gain of the measuring system, and the compression of the solvent. The corrected data appear to fall about a straight line, indicating that the activation volume model may be applied here, as in the case of the photoreaction. A linear fit performed by eye yields a value of 13.5 cc/mole for the activation volume in this case.

The dependence of photochemical quantum efficiency on pressure for the ethanolic solutions is shown in Figure (10). A straight-line fit by eye yields a value of 5.11 cc/mole for the activation volume.

The bimolecular recombination constant in ethanolic solution does not show the exponential quenching with pressure which appears to characterize the preceding sets of kinetic data.

Figure 8. The dependence of photochemical quantum efficiency (ϕ) on pressure, for aqueous solutions.

Figure 9. The dependence of the bimolecular recombination rate on pressure, for aqueous solutions. The open squares (fitted by the broken line) are corrected for gain variation and for solvent compression.

Figure 10. The dependence of photochemical quantum efficiency on pressure for 20% ethanolic solutions. The "best line" through the analogous aqueous data is shown for comparison.

The raw data, and the data points corrected for compression and gain, are shown in Figure (11). A straight line has been fitted, by eye, to the corrected data. Over the pressure range of these measurements, the fitted line follows closely the inverse viscosity of the solvent.

For all kinetic measurements, the practical upper limit on applied pressure was reached when time-constants became so long that interference from secondary chemical reactions and from instrumental drift became significant.

Figure 11. The dependence of the bimolecular recombination rate on pressure, for 20% ethanolic solutions. The open squares (fitted with the broken line) include corrections for compression, and variation of gain.

5. DISCUSSION

5.1 Introduction

The object of this project was the construction of an apparatus for the measurement of photoconductivity in liquids pressurized up to ten kilobars, and the demonstration of its feasibility.

The measurement of photoconductivity provides a probe of light-induced ionic reactions which is extremely sensitive, and which can easily be adapted to high-pressure cells. By far the richest field for future application of this technique is the photoionization of transition metal complexes and aromatic electron donor molecules in solution, and the photolysis of aromatic donor-acceptor complexes. Numerous authors have reported photoconductivity studies, at one atmosphere, of aromatic donors, and of both ground-state donor-acceptor complexes, and exciplexes. Due to the rapid relaxation of these systems, constant illumination provides an extremely small steady-state ionic concentration. A much greater transient ionic concentration is attainable by the flash technique, but in both cases the use of high-powered lasers is mandatory in order to obtain quantitative data.

To demonstrate the practicability of the pressurized liquid photoconductivity apparatus, a chemical system was chosen whose long relaxation time allowed the use of a conventional light source; this system is the ferrocyanide ion in dilute

aqueous solution. While this system was chosen primarily for its expediency, the data generated by the present study have nevertheless proven capable of a simple physical interpretation; on this basis, certain arguments concerning photochemical reaction mechanism can be made.

The experimental data represent the conductivity change of the sample as a function of time after the onset of illumination, and after its cessation. The former behavior is described by an exponential function,

$$Y = P_1 + P_2 \exp.(-P_3 t)$$

while the latter is described by a bimolecular kinetic expression:

$$Y = P_1 + P_2/(1 + P_3 t) \quad .$$

The pre-exponential factor, and the rate constants for both the pseudo-first-order, and the second-order, processes, were found to be pressure-dependent.

In order to distinguish between viscosity effects and other effects of pressure, a pair of solvents were used whose viscosities behave very differently under pressure. The first solvent is pure water, and the second is a 20 mole-percent aqueous solution of ethanol. While the behavior of the pseudo-first-order rate constant is markedly similar in both solvents, the pre-exponential and the bimolecular rate-constant show significant differences.

This discussion will be addressed first to the pressure-dependence of the pre-exponential factor in alcoholic and aqueous solutions. The quantum efficiency of the photochemical reaction will be discussed next, and an interpretation will be presented based on the consideration of activation volumes. Finally, the bimolecular recombination kinetics will be discussed, and an interpretation based on activation volumes will be presented.

5.2 The Pre-Exponential Factor

The pre-exponential factor is of positive sign in the alcoholic solution, but of negative sign in the aqueous solution. On the basis of exhaustive pH and conductivity measurements (Appendix I), the author has determined that the explanation for the discrepancy lies in the fact that the pH of the aqueous solution is about 6, due to the presence of a small concentration of carbon dioxide as carbonate ion. When cyanide is released by the photoreaction, neutral hydrogen cyanide is formed. A charge is lost from the complex ion, and the number of highly mobile hydronium ions is reduced. Thus the conductivity decreases rather than increasing.

Despite the difference in sign, the pre-exponentials in both alcoholic and aqueous solutions show pressure-induced changes which are amenable to simple physical explanation, and which can, in part, be ascribed to the same mechanisms. The following discussion therefore focusses on changes induced

by pressure in the absolute value of the pre-exponential in both systems.

The pre-exponential factor is proportional to the saturation level photocurrent. If recombination effects can be neglected, then in the first approximation this quantity is proportional to the product of the ionic mobility times the concentration of sample. In alcoholic solution, the recombination is very slow, even at one atmosphere; consequently, for brief exposures, this approximation is valid. In fact, the pressure-dependence of the pre-exponential in alcoholic solutions was found to parallel the reciprocal viscosity, which is the main pressure-dependent influence on ionic mobility. The concentration of sample increases slightly with pressure, due to compression of the solvent; in the alcoholic solution, though, this effect is overwhelmed by the viscosity effect.

Various complications arise in discussing the pressure variation of the pre-exponential in aqueous solution. The viscosity change is much smaller in this case, and, while still significant, it no longer overwhelms the compression effect, which, consequently, must also be considered (Table (2)).

The compression and the viscosity increase at about the same rate from one atmosphere to 2 kilobars, effectively cancelling each other in that range; the large initial rise in the absolute magnitude of the pre-exponential must therefore be due to other effects. Between 2 and 4.5 kilobars, the viscosity increases more rapidly than the compression, but the

Table 2. The compression and viscosity of pure water and of 20 mole-percent ethanol as a function of pressure (After Reference [21]).

	Pressure (kbar)	Compression ($-\Delta V/V_0 \times 100$)	Viscosity (cP)
Pure Water:	.34	1.57	0.855
	.68	2.89	0.849
	1.04	4.18	0.811
	1.37	5.27	0.814
	1.74	6.39	0.787
	2.11	7.41	0.814
	2.46	8.29	0.840
	2.79	9.17	0.853
20% Ethanol	.37	1.60	2.604
	.69	2.88	2.766
	1.02	4.05	2.892
	1.36	5.13	3.038
	1.73	6.24	3.194
	2.08	7.15	3.317
	2.41	8.01	3.454
	2.81	8.89	3.610

pre-exponential continues to grow.

Above 4.5 kilobars, additional compression of the solvent is very slight, and the pressure-dependence of the pre-exponential is roughly parallel to the reciprocal viscosity.

The magnitude of the pre-exponential goes through a maximum around 3 kilobars, and then slowly falls off. It is interesting to compare this behavior with that of the viscosity of liquid water at zero Celsius degrees, which falls to a minimum near one kilobar, and then rises in the expected way [22]. The room-temperature viscosity of pure water does not show this anomaly; however, a maximum has been observed at one kilobar in the limiting molar conductance of potassium chloride in aqueous solution at 45 degrees. Hamann [13] has applied the postulate of local "freezing" of the solvent about dissolved ions to propose that this behavior is essentially identical to the low-temperature anomaly in pure water. In view of this argument, it is likely that a small but significant contribution to the initial rise in the magnitude of the pre-exponential is made by a decrease in the local viscosity.

Pressure is known to enhance the dissociation of weak electrolytes, such as potassium ferrocyanide [22]. Conductivity studies by the author of ferrocyanide solutions at one atmosphere have shown little difference in the degree of dissociation for dilute solutions in water, and in twenty-percent ethanol. It is therefore doubtful that enhancement of dissociation in the aqueous solution could explain the large difference between the

two systems observed at pressures below 3 kilobars; furthermore, this argument would predict an increase, rather than a decrease, in the absolute magnitude of the pre-exponential in alcoholic solution relative to that in water.

It has been shown by the author (Appendix I) that the sign and magnitude of the pre-exponential in the aqueous samples is very sensitive to pH, and that the pressure data were obtained with samples containing enough dissolved carbon dioxide to bring the pH (at one atmosphere) down to about 6. Under these conditions, the absolute magnitude of the pre-exponential was found to be very sensitive to negative changes in the pH. We may expect, then, that an increase with pressure in the concentration of hydrogen ions will cause an initial rise in the magnitude of the pre-exponential. Doubling of the hydrogen-ion concentration in three kilobars would suffice, according to the findings reported here, to explain the observed doubling of the pre-exponential in that range.

The electrical conductivity of pure water is known to increase roughly tenfold in 12 kilobars, reflecting a similar increase in intrinsic dissociation in that pressure range [13]. Moreover, borate, phosphate, and (of particular interest to this discussion) carbonate buffers have been found to show a doubling of the hydrogen ion concentration in 3 kilobars [23]. This evidence makes plausible the proposed shifting of chemical equilibria in the system under study.

Finally, the approximation introduced by disregarding the recombination must be considered. While pressure rapidly reduces the recombination rate until, above 3 kilobars, it can safely be disregarded in the measurement of the pre-exponential, the saturation photocurrent at the lowest pressures may be limited by recombination rather than by exhaustion of the reactant. The experimental accuracy was not such as would justify the detailed mathematical analysis necessary to eliminate this source of error.

Our conclusions follow, regarding the variation with pressure of the absolute magnitude of the pre-exponential in aqueous solution: The sharp rise going from one atmosphere to two kilobars is governed by roughly equal contributions from hydrogen-ion effects and from kinetic effects, with a small contribution due to a minimum in the local viscosity near one kilobar. Over the range from two to four kilobars, the chemical effects begin to level off, and the viscosity change begins to dominate. Above four kilobars, the viscosity effect dominates the limiting photocurrent.

5.3 The Quantum Efficiency

The pressure-derivative of the logarithm of the photochemical quantum efficiency was found to be constant, within experimental error. We cannot conclude that the activation volume is independent of pressure, for at low pressure, where the quantum efficiency is considerable, the relationship between quantum efficiency and microscopic rate-constant deviates from

linearity. In the absence of a compensating correction, that is, in the high-pressure limit, the volume of activation was found to be 6.15 cc/mole in the aqueous solution, and 5.11 cc/mole in the ethanolic solution. Using the most widely accepted literature value of 0.2 [7] for the photochemical quantum efficiency in aqueous solution, a corrected value of 7.7 cc/mole was found for the activation volume in aqueous solution at one atmosphere. The quantum efficiency in ethanolic solution was not discussed in the literature; however, an estimated value of 0.4 was found by the author on the basis of comparative measurements at one atmosphere. Using this value, the corrected value for the activation volume in twenty-percent ethanolic solution at one atmosphere was estimated to be 8.7 cc/mole. The corrected one-atmosphere values in both cases exceed the value in the high-pressure limit; this is consistent with the usual decrease in activation volume with increasing pressure as the solvent becomes less compressible. For comparison, the isothermal compressibility of water at 25 degrees C decreases by about 45% in the range from one atmosphere to three kilobars, and decreases much more slowly thereafter. The compressibility of 20% ethanol has very similar behavior to that of pure water (Table (2)).

The similarity between the values obtained for aqueous and ethanolic solutions suggests that the same mechanism for ligand exchange operates in both case. The results will be discussed in terms of the associative (A), dissociative (D), and interchange (I_a or I_d) mechanisms described in Section 2.2.

Since an increase in volume accompanies the activation step, the A mechanism, wherein bond-formation would occur between the complex and a solvent molecule, is positively ruled out.

If a D mechanism were in operation, the volume effect would be controlled by the release of a cyanide ion. In that case, the quadruply charged ferrocyanide anion would lose a single charge to the newly created cyanide ion. In general, when a charged ligand is exchanged for a solvent molecule, the electrostatic compression of the solvent around the ions dominates the activation volume; since this term is proportional, in the first approximation, to the square of the ionic charge [24], this effect should be large for the highly-charged ferrocyanide ion.

The measured activation volume in aqueous solution of 6-8 cc/mole is positive, but small, in view of the high charge of the ferrocyanide ion. Consequently, the breaking of the metal-to-cyanide bond is indicated as the most important rate-determining process, but the simultaneous participation of an incoming water molecule in an I_d mechanism seems highly probable. The compressibility of water and of twenty percent ethanol are very similar; the significant difference between the activation volumes in the high-pressure limit in the two solvents cannot be explained on this basis. Furthermore, the difference in the dielectric constants of the two solvents is inadequate, based on the simple dielectric theory, to explain the discrepancy. A possible explanation is greater participation by the incoming water molecule, in the ethanolic solution. The difference between local and bulk solvent conditions must be more marked in the ethanolic case, because of the greater affinity of the ions for water over ethanol.

Thus, specific effects may arise in that case which cannot be predicted by simple theory.

5.4 The Recombination

The bimolecular recombination constant, for the dark-reaction in water, was found to fall off with pressure at a rate consistent with an activation volume for recombination of 13.5 cc/mole. This value is three-fourths the molecular volume of water, namely, 18.0 cc/mole, and is strongly indicative of a D mechanism. For dissociation of a water molecule from the complex, no charge effects obtain, and the five-coordinated activated complex should occupy the same volume as the stable six-coordinated complex [25]. Kelm and Palmer [26] have pointed out that due to electrostatic compression about the complex ion, the molecular volume of the solvent in the second and third coordination spheres is significantly less than that of the bulk solvent. The D mechanism is consistent with the majority of thermal ligand-substitution reactions of octahedral complexes that have been studied. In twenty-percent ethanol, the bimolecular rate-constant appears to vary linearly as the reciprocal viscosity. This behavior suggests a diffusion-limited process. That this is plausible is shown by the following argument:

Shirom and Stein [7] estimated the bimolecular rate-constant in aqueous solution to be 5×10^6 /mole-sec. This is about an order of magnitude slower than the theoretical threshold for diffusion-control. In going from aqueous solution to twenty-percent ethanol, the viscosity is tripled, and the dielectric constant is reduced by twenty-five percent. As a

result, both the ionic diffusion coefficient, and the electrostatic shielding between the similarly charged reactants, are reduced. Simple estimates predict an order-of-magnitude decrease in the diffusion-limited rate [27]. Comparative rate measurements performed by the author at one atmosphere are consistent with this prediction. Thus, the diffusion-limited rate is lowered into a range where it can compete for control of the reaction kinetics.

5.5 Future Capabilities

The apparatus and techniques described here are applicable to any photochemical reaction which involves redistribution of charge in the creation of solvent-stabilized transients, and where the number of possible photochemical products is very limited. As more information is gathered, through conventional means, about the photochemistry of transition metal ions, the variety of reactions to which the present technique is applicable will certainly increase.

The present study, as an exploratory investigation of a novel apparatus, was confined to available laboratory light sources and detection instruments. The range of problems which can be approached using the photoconductivity cell described here could be greatly expanded by the use of high-power pulsed lasers, and continuous-spectrum kilowatt lamps with suitable monochromators. It is appropriate to discuss here some of the liquid photoconductivity research of recent

years which could benefit by extension to high pressure using the cell which is described in this work.

Pulsed laser excitation provides the most sensitive photocurrent measurements. Under conditions of fast recombination of photogenerated carriers, flash-generated transients may have amplitudes as much as 10^6 times the steady-state amplitude at the same incident light intensity. Typically, a flash of 2-10 microseconds duration and 10^{16} absorbable photons is used. Fast detection circuitry is essential; normally, the photocurrent signal is passed through a small measuring resistor, and the voltage drop applied directly to an oscilloscope with a fast input amplifier. A d.c. voltage is applied between the electrodes of the photoconductivity cell. Because of the short timescale of this type of measurement, both polar and nonpolar solvents are permissible [28].

The high-pressure photoconductivity cell has been used by the author at one atmosphere to measure the photoionization spectrum of an aromatic electron donor in several non-polar solvents. A field of 1 kilovolt/cm was applied between the electrodes. The light source was a 150 watt xenon lamp with a grating monochromator. The current detector was a Keithley 427 current-to-voltage converter, operated at a gain of 10^{11} volts/ampere, and a time constant of 300 msec. Current resolution of 10 picoamperes was obtained, but useful measurements could not be made above 1 kilobar, due to attenuation of the signal.

Solute photoionization studies have concentrated mainly on the aromatic electron donor N,N,N',N'-tetramethyl-p-phenylene diamine (TMPD). The ionization threshold of this compound is sufficiently low to permit both monophotonic and biphotonic ionization in the near ultraviolet, producing an electron and the relatively stable monocationic Wurster's Blue cation. Steady-state measurements have been used to determine the ionization threshold in a variety of polar and non-polar solvents, and kinetic and quantum-yield measurements have been made using pulsed laser excitation.

Takeda, et al. [29] reported the measurement of ionization thresholds using two steady-state light sources. In this way, the thresholds for ionization of both the ground state, and of the lowest excited triplet state (which is the intermediate in 2-photon ionization of TMPD) were measured. It would be of considerable scientific interest to vary the pressure in this situation, observing the relative changes in the energy separation between the ionized state and, respectively, the ground state and the lowest triplet state.

Holroyd [30] measured steady-state photoionization spectra of TMPD in a variety of solvents. A large solvent shift in the photoionization threshold was observed, which he interpreted in terms of the energy of the excess electron state in the solvent, and the polarization energy of the solvent with respect to the cation. By introducing the variation of pressure

to this study, the effect of pressure on the electronic structure of the solvent, and specific solvation effects, may be elucidated. Indeed, a variety of dissolved electron donors might be studied in this way, with a standard photocathode serving as a basis for comparison, in order to separate out the solvation effects.

Tamir and Ottolenghi [31] used pulsed laser excitation in an effort to elucidate the mechanism for biphotonic ionization of TMPD in non-polar solvents. Two models were considered. In one, two donor molecules in the excited triplet state collide, producing one ground state molecule and one ionized molecule. In the second model, a single molecule is involved; the second absorbed photon leads to the ionization of the excited triplet. The second model was supported by concentration and dosage effects. If, in analogous systems, the hypothetical bimolecular kinetics of the first model are diffusion-limited, then this mechanism can be distinguished by the change in viscosity, and hence, molecular diffusion coefficient, induced by pressure.

Houser and Jarnagin [32] and Imura, et al. [33] measured the flash photoionization kinetics of TMPD in solution. On the basis of these data, arguments were made regarding the escape probability of the photoelectron from the Coulomb field of the parent cation, and the factors affecting it. The application of pressure would tend to increase the escape probability by increasing the dielectric constant of the solvent, but would

also have the opposite effect by increasing the density of the solvent, and thus decreasing the thermalization distance of the ejected electron. On the other hand, since recombination involves thermalized electrons only, the pressure effect on the recombination kinetics is expected to depend on dielectric constant, and solvent viscosity. By varying solvent and pressure, basic information may be obtained regarding charge-carrier pairs in solution.

A number of electron donors besides TMPD have been subjected to photoionization photoconductivity studies in solution. Nakato and Tsubomura [34] studied optical transitions to the Rydberg-like and ionized states of 1,1',3,3'-tetramethyl-2,2'-biimidazolidinylidene. They showed a strong correlation between the appearance of photoconductivity and the quenching of fluorescence from the higher energy excited states, with the ionization threshold showing a definite solvent shift. The relative variation with pressure of the highly excited bound electronic energy levels, and the excess electron level of the solvent, is an interesting problem which can be approached through the comparison of fluorescence and photoconductivity excitation spectra. Tang, et. al. [35] studied the pulsed photoconductivity of chlorophyll-a films in contact with a non-polar solution of the chlorophyll-a monomer. The presence of the monomers appeared to enhance the yield of charge-injection into the solution, possibly by providing a resonance

charge-transfer path for the transport of charge away from the film-solution interface. The identity of the carriers in solution was not determined. Many possible mechanisms for charge generation and transport could be at work here, in the elucidation of which pressure might be useful.

Other organic solutions of electron donors which have been found to exhibit photoconductivity as a result of solute photoionization include solutions of beta carotene, indole, and various substituted benzene compounds.

Ion production by the dissociation of exciplexes in polar solvents has also been studied photoconductimetrically. Kawada and Jarnagin [36], and Gary, et. al. [37], using pulsed excitation, reported kinetic evidence for ion production through bimolecular triplet-triplet encounters of excited aromatic hydrocarbons. Nakato, et. al. [38] reported a one-photon ionization process for TMPD in ethanol, via electron exchange between the excited singlet of TMPD and a ground state naphthalene molecule. Taniguchi and Mataga [39] studied photocurrent transients arising from the flash photolysis of aromatic hydrocarbon-dimethylaniline systems. They reported kinetic evidence that ion radical formation occurs mainly from the non-relaxed state of the ion-pair immediately after electron transfer and before the relaxed exciplex state is formed. Some ionic dissociation from the relaxed exciplex state was also observed. Since pressure would probably stabilize the solvated ions relative to the solvated ion-pair, it would be interesting

to see whether pressure increased the photocurrent from the relaxed exciplex. This could be determined by comparison of the "fast" and "slow" parts of the photocurrent transient.

Photoconductivity studies of ground-state charge-transfer complexes in polar solvents have also been reported. Imura, et al. [33] measured photocurrent transients due to the flash photolysis of several organic electron donor-acceptor complexes. They concluded that the excited charge-transfer state could dissociate, forming either a solvated ion-pair, or a pair of independent, solvated ions. Shimada, et al. [40] used fluorescence decay and laser-excited photocurrent measurements to determine that ionic dissociation of the complex between tetracyanobenzene and benzene occurs in the excited Franck-Condon state. Using flash photolysis and photocurrent transient measurements, they found two mechanisms for the ionic dissociation of organic donor-acceptor complexes. Depending on the reactants, solvent, and temperature, dissociation could be from either the lowest excited charge-transfer singlet state, or from the lowest excited triplet. It would be an interesting exploratory study to see how the relative yields from these two mechanisms are manipulated by pressure.

This discussion provides a sampling of the variety of high-pressure solution photoconductivity problems which could be attacked with the present cell and appropriate auxiliary equipment.

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APPENDIX I

The photocurrent amplitude was found to be negative in aqueous samples, and positive in alcoholic samples. In addition, solutions of potassium ruthenocyanide (the Ru(II) and Fe(II) ions are isoelectronic) showed a small, positive photocurrent amplitude in both aqueous and ethanolic solutions. For a ruthenocyanide concentration of (4.8×10^{-4}) M, the measured photoconductivity amplitude was $+0.36 \mu\text{Mho}$ in pure aqueous solution, and $+0.13 \mu\text{Mho}$ in 20% ethanol.

A series of electrochemical measurements was undertaken in an effort to account for the difference in sign. The chemical effects which were investigated were ion-association effects and pH effects. The rationale behind the ion-association investigation was that whereas the photoaquation in water is represented by

the analogous reaction in a solvent of lower dielectric constant, such as 20% ethanol, might proceed according to

Thus, regardless of secondary reactions of the cyanide ion, the freeing of a potassium ion in the ethanolic system would correspond to a large positive contribution to the

conductivity change. If potassium ruthenocyanide could be shown to exhibit greater ion-association in aqueous solution than potassium ferrocyanide, the same explanation would apply to the direction of the ruthenocyanide photoconductivity.

The purpose of the pH measurements was to explore the acid-base equilibria between residual carbonic acid in the solvent, and the cyanide ion, which is a strong base, as well as between carbonic acid and the parent complexes, which are weak bases.

Ion-association effects are identified by a characteristic "elbow" in the plot of molar conductance vs. dilution of an electrolyte. The data shown in Tables I.1 and I.2 show that the degree of dissociation of potassium ruthenocyanide is identical to that of ferrocyanide, and that evidence for ion-association is absent from both sets of aqueous data, as well as from the data on potassium ferrocyanide in 20% ethanol.

Table I.3 indicates a residual pH of about 6 due to the presence of dissolved carbon dioxide in the solvent water as prepared for the photoconductivity measurements. The same table shows that ruthenocyanide is more extensively protonated than ferrocyanide, and that whereas the ferrocyanide sample solutions are slightly acidic, the ruthenocyanide samples are neutral or slightly basic. Table I.4 shows a definite increase in the pH of ferrocyanide solution as the ethanol concentration is increased. Since the measured effect is much

greater than the effect that the addition of ethanol has on the ionization of pure water, the pH most likely increases due to enhanced protonation of the ferrocyanide ion, and to shifting to the left, as the ionizing power of the solvent decreases, of the equilibrium.

Since hydrogen cyanide is an extremely weak acid ($K_a = 4.83 \times 10^{-10}$) we may assume that the cyanide ion which is released by the photochemical reaction is almost completely protonated in every case. Consideration of the multiple chemical equilibria in the slightly acidic aqueous solutions leads to the conclusion that the hydronium ion concentration remains approximately constant, and that the net result of releasing a cyanide ion into the solution may be represented by

Thus, one unit of electrical charge with the mobility of the ferrocyanide ion (equivalent ionic conductance of 111) is lost, due to the photoreaction, and one bicarbonate ion is produced (equivalent ionic conductance of 45). The net result is a conductivity decrease.

In 20% ethanol, and in the ruthenocyanide solution, the secondary reaction of the cyanide ion which dominates the conductivity change is

Thus, a unit of charge with the mobility of ferrocyanide is lost, and a highly mobile hydroxyl ion is produced (equivalent ionic conductance of 198). An increase in conductivity is the result.

In aqueous solution at very low pH, the secondary reaction dominating the conductivity change would be

In this case, a unit of charge with the mobility of ferrocyanide is lost, as well as a hydronium ion (equivalent ionic conductance of 350). As the pressure on a slightly acidic solution is increased, one would expect the last process to make an increasing contribution to the photochemical conductivity change.

The data in Table I.5 support the above conclusions.

The solvent water which was used in preparing the samples which provided the data in Tables I.1, I.2, and I.5 was treated as follows: Freshly distilled and deionized water was boiled and cooled in an inert atmosphere. Immediately upon mixing, all solutions were purged for 30 minutes with argon.

Table I.1

Effect of concentration on molar conductance
for aqueous solutions

Dilution (Liters/Mole)	Λ	
	$K_4Fe(CN)_6$	$K_4Ru(CN)_6$
1.0×10^1	320	
3.0×10^1	250	340
9.0×10^1	400	380
2.7×10^2	460	480
8.1×10^2	520	530
2.4×10^3	580	520
7.3×10^3	610	610
2.2×10^4	590	570
6.6×10^4	700	690

Table I.2

Effect of potassium ferrocyanide concentration on
molar conductance in 20 mole-percent ethanol

Dilution (Liters/Mole)	Λ	
	Trial 1	Trial 2
2.0×10^2	100	110
6.0×10^2	130	130
1.8×10^3	160	150
5.4×10^3	190	180
1.6×10^4	200	210
4.9×10^4	210	250

Table I.3

Effect of electrolyte concentration on pH of aqueous solution

Molar Concentration	$K_4Fe(CN)_6$			$K_4Ru(CN)_6$	
	Trial 1	Trial 2	Trial 3	Trial 1	Trial 2
10^{-2}	6.8	6.8	6.7	8.7	8.5
10^{-3}	6.4	6.3	6.3	7.5	7.8
10^{-4}	6.1	6.0	5.9	6.4	6.6
10^{-5}	5.8	5.7	5.6	5.9	6.0

Table I.4

Effect of ethanol concentration on pH of $2.4 \times 10^{-4} \text{M}$
solution of potassium ferrocyanide

Mole-Percent Ethanol	Trial 1	Trial 2
0	6.8	7.0
5	7.3	7.2
10	7.4	7.5
15	7.6	7.7
20	7.7	8.0

Table I.5

Effect of pH on limiting photoconductivity amplitude
of 2.4×10^{-4} M aqueous solutions of
potassium ferrocyanide

pH of Sample	Limiting Photoconductivity Amplitude (μ Mho)	Comment
4	-4	CO ₂ was bubbled through pure solution for 5 minutes. Cell was kept in CO ₂ atmosphere during exposure.
7	-0.2	Pure solution thoroughly purged with Argon. Cell kept in inert atmosphere.
9	-0.03	pH adjusted with KOH. Inert atmosphere maintained.
12	+0.5	NH ₃ bubbled through pure solution for 5 minutes. Cell kept in ammonia atmosphere during exposure. Qualitatively similar results were obtained when pH was adjusted with KOH rather than NH ₃ .

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