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FLASH PHOTOLYSIS AND PULSE RADIOLYSIS IN COORDINATION CHEMISTRY

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The title of the present Bressanone Conference confirms the interest of the research chemist in the stability of coordination compounds and in their reaction mechanisms under various experimental conditions.

Many times in the past, at such meetings, we have heard the sentence: "the reaction is instantaneous" or "the reaction goes too fast to be followed kinetically". However, as techniques and methods capable of producing and studying more and more labile chemical species are developed, the horizons of chemical kinetics are constantly being extended. The mechanisms of many chemical reactions are steadily being elucidated, even those that until now seemed definitively studied. No chemical reaction today may be considered as "immeasurably fast". Modern electronics provide an extraordinary range of sensitivity and time resolution so that current experimental technique extends to reactions with half-times approaching those for molecular vibrations and rotations. The specification of a chemical mechanism requires a knowledge of all the individual or elementary steps in the overall chemical reaction and an understanding of each elementary step on a molecular basis (i.e., study of transient species).

Only with fast reaction techniques can elementary processes be fully resolved but two experimental problems arise in connection with the direct investigation of very fast reactions. First, the reaction must be initiated in a time that is short in comparison with the overall reaction time; second, a significant parameter of the reacting system must be recorded, after initiation, in such a manner that useful information regarding the mechanism and the kinetics of the reaction can be derived from it.

There are several general methods for bringing about a chemical reaction, but for very fast reactions some of the methods have fundamental limitations. The absorption of energy by a system from radiation, light quanta, or accelerated particles, is the basis of both flash photolysis and pulse radiolysis. In pulse radiolysis, excitation and ionization by electron impact with a very soft pulse of high-energy electrons replaces the process of photoexcitation by a photoflash. With these techniques, the rapid absorption of energy serves to produce unstable molecules (ions, excited states or free radicals) generally very far from their equilibrium states. The fate of these molecules as the system proceeds to equilibrium can be studied directly, or the unstable molecules can be used to initiate reactions of interest.

The rapid rise in laser technology has given considerable impetus to this area, both in generating rapid perturbations and in following the time course of the reactions. The time resolution of these methods is typically in the microsecond range, but nanosecond and even picosecond resolution has been achieved. The published data indicate that the two techniques considered here hold an important position in the study of fast reactions (range of applicability between log[time] (sec) = 0 ÷ −11, −12).

In 1968 the Italian National Research Council founded a new Laboratory for radiation research, called Photochemistry and High Energy Radiation Laboratory, the FRAE. Its main field of research was the study of any kind of transient species or transient phenomena produced by ionizing or other radiations. Pulse radiation sources of high intensity and short duration, and suitable detection methods, were so set up to meet the experimental requirements.

The two techniques discussed in this section have been well reviewed; I refer for instance to two very recent papers by G. Porter [1] and by L.M. Dorfman [2]. It is sufficient therefore to point out here that the two important characteristics of these methods are the nature of the energy deposition in the system and the time scale for this energy deposition. Only by the combination of favourable features for both these characteristics are the two methods of great value in the study of a wide variety of mechanisms of interest to the coordination chemist.

A first comment to be made is that the conditions of the systems are usually quite different for the two techniques. While for the photoexcitation in solution, the solvent chosen is usually transparent to the wavelengths of the photoexciting light, no substances are transparent with respect to absorption of energy from high-energy electrons. In this case the deposition of energy in the absorber system is Coulombic and therefore the energy deposition will depend on the electron density of the absorber molecules, so that in dilute solutions, the electron energy will be given almost entirely to the solvent molecules and not to the solute.

EXPERIMENTAL METHOD

A typical irradiation arrangement consists of three parts:

(1) A photolysis flash or an electron accelerator for producing a short pulse of light or particle of very high intensity.

(2) A reaction vessel.

(3) An arrangement for physical detection and estimation of transient intermediates. Absorption spectroscopy is the usual method adopted. The absorption spectrum can be investigated in two ways, and a single experiment can serve to record either the whole range of wavelengths at a single time or, alternative-

ly, a single wavelength over all times. The first approach is called flash spectroscopy, the second one kinetic spectrophotometry. Other methods for the detection of transient species, such as conductimetry, polarography and rapid ESR absorption measurement have been successfully applied in Pulse Radiolysis.

Flash photolysis equipment is now manufactured commercially by several companies, and ranges from simple apparatus, suitable for teaching and the study of millisecond transient, to advanced equipment for research work equipped with pulsed laser sources.

For radiolysis, microwave linear accelerators (LINAC) are the most common instruments. These are pulsed-electron accelerators operating from a supply of high-voltage d.c. power, which is converted, by means of a tuned amplifier such as a klystron, into pulses of radio-frequency power. These pulses are then coupled to cylindrical wave guides in which the acceleration takes place. Electron from a high-current electron gun are injected into the microwave field in the wave guide, the number of sections in the wave guide being determined by the electron energy desired.

Repetitive electron pulses are produced with a maximum duration of about 1—5 μsec, which is continuously variable down to the nanosecond region, at a repetition rate up to about 500 pulses sec^{-1}; the FRAE Laboratory is equipped with one of these accelerators. Single pulses are most commonly used in pulse radiolysis, just as a single flash is used in flash photolysis, but repetitive pulses have been used in the stroboscopic time-sampling method for picosecond time resolution. For the most part the detection methods are similar to those used in flash photolysis.

The pulse radiation sources first planned for the FRAE laboratory were the two Febetron 705 and 706 (manufactured by Field Emission Corporation). The first delivers electron beams at 600 keV and the second at 2 MeV. They operate by discharging a bank of capacitors simultaneously through a Marx surge circuit, producing a pulse with a duration of several tens of nanoseconds. This is then shortened by an oscillatory discharge circuit adapter. A field emission cathode permits the delivery of very short pulses at extremely high currents ranging from hundreds to thousands of amperes.

Under a given set of operating conditions, these machines deliver a single pulse of fixed energy, current and duration. Because of the charging time of the capacitors the pulse can be repeated only with an interval of several minutes or more between pulses. The principal advantages of the Febetrons are their relatively low cost and high pulse current. Since the machine does not provide repetitive pulses, the "average dose" delivered over extended periods is very low; therefore the shielding requirements, and hence shielding costs, are relatively modest. It has recently been found that the pulse from this machine can be substantially focussed and narrowed by subjecting the beam to a magnetic field [3].

GENERAL EXAMPLES OF COORDINATION SYSTEMS STUDIED BY NANOSECOND FLASH PHOTOLYSIS OR PULSE RADIOLYSIS

Flash Photolysis and Pulse Radiolysis give interesting information on the behaviour of excited states of chemical molecules, differing in some aspects, from the information gained by the usual thermal chemistry.

The present importance attached to the electronic excited states produced in the course of the usual thermal reactions is of great significance. Such chemically produced excited states are (as a rule) identical to light produced excited states, and they undergo molecular transformations expected of such states ("photochemistry without light"). The excited states can also be used in energy transfer experiments [4].

Many papers have been published dealing with the flash photolysis of coordinations compounds. As far as pulse radiolysis is concerned, many of the published papers deal only with the nature of the primary processes and with reactions between primary species (such as e_{aq}^- and OH radicals) and dissolved solute. The number of investigations in which pulse radiolysis has been exploited by inorganic chemists for those areas of coordination chemistry for which it is particularly suited, i.e., for the possibility of explaining some kinetic or mechanistic problem of general interest, is much smaller.

It is the purpose of this article to report some of these applications with an indication of the particular advantages in each case, or at least of the feasibility of the technique, and some recent results which have been obtained at the FRAE Laboratory. The emphasis will be on Pulse Radiolysis.

Following Balzani's example [5], I shall classify the reported reactions in four groups: Substitution, Isomerization, Redox and Ligand. All of them may be encountered in Flash Photolysis, and sometimes together in the same compound. Unlike many other techniques for the study of fast reactions in solution, the perturbation by the electron pulse is fundamentally an oxidation—reduction perturbation.

The irradiation of neutral water leads to the formation of several reactive transients, among them the hydrated electron, as well as the molecular products H_2 and H_2O_2:

$$H_2O \rightsquigarrow OH, e_{aq}^-, H, H_3O^+, OH^-, H_2, H_2O_2 \qquad (1)$$

The hydroxyl radical exhibits strong oxidizing properties; the hydrated electron and the hydrogen atom (formed with a yield only one-fifth that of e_{aq}^-) exhibit reducing properties. The various reactions among these species account for the overall chemical effects of the irradiation of water. The aquated electron and the hydroxyl radical have such extreme reduction potentials in water (—2.77 and +2.3 V, respectively) that for nearly all substrates one or the other can bring about oxidation—reduction processes.

Unlike the hydrated electron, which exhibits a very strong broad structureless optical absorption band in the visible to near-infrared region of the spectrum (ϵ_{700} = 15.000), the hydroxyl radical in water does not exhibit conveniently accessible optical absorption, with the result that its reactivity cannot be determined readily by direct observation of the species itself. However, rate constants for many hydroxyl reactions have been determined in other ways, primarily by observation of the formation of the transient product or the stable product of the elementary reaction of hydroxyl, as well as by competitive kinetics using as reference reaction a hydroxyl reaction for which the rate constant is known absolutely.

Substitution reactions

Substitution reactions of the extremely labile Cu^{2+}_{aq} (d^9) and Cr^{2+}_{aq} (d^4) ions are very fast. The rates of water exchange on these ions are greater than 5×10^9 sec^{-1} and ligand substitution processes are correspondingly fast.

Pulse radiolysis may be used to measure substitution rates in systems of this kind in two ways. The equilibrium between the metal ion and the ligand can be perturbed by converting some of the metal ions to another oxidation state, or, the metal ions in the required oxidation state can be formed radiolytically in the presence of the ligand. In the first case, for the equilibrium between Cr^{2+}_{aq} and ligand L (reaction (2)), the concentration of Cr^{2+} is suddenly reduced

$$Cr^{2+} + L \rightleftharpoons CrL^{2+} \qquad (2)$$
$$Cr^{2+} + OH \rightarrow Cr^{3+} + OH^- \qquad (3)$$

after the electron pulse because of reaction (3), and then the return of reaction (2) to the new equilibrium position can be followed. The kinetic analysis is complicated because of the very similar rates of reactions (2) and (3). An equivalent approach, which is more easily interpreted kinetically, is to use e^-_{aq} to reduce Cr^{3+} ions in the presence of the ligand, generating Cr^{2+} ions which then react by reaction (2). The complication in this method is the possible interference from OH radicals.

The equilibria of a number of labile Fe^{III} complexes have been disturbed in this way, and the return to equilibrium followed. The rate constants obtained are in good agreement with those measured by stopped-flow methods.

Electron transfer reactions

Pulse radiolysis is frequently well suited for the study of very rapid electron transfer or oxidation—reduction reactions because of the ease with which one of the reactants can be generated. The reaction between V^{2+}_{aq} and Co^{3+}_{aq} ions (4)

$$V^{2+} + Co^{3+} \rightarrow V^{3+} + Co^{2+} \qquad (4)$$

is too fast for conventional stopped-flow measurements and the rate constant could only be obtained by competition methods. The rate constant is ca.

10^6 l mole^{-1} sec^{-1} and the reaction can be followed directly if pulse radiolysis is used to generate the Co^{3+} ions. Both V^{2+} and Co^{2+} ions react with OH radicals, to give V^{3+} and Co^{3+}, with rate constants of ca. 10^{10} and 10^8 l mole^{-1} sec^{-1}, respectively. In a solution containing N_2O, 10^{-1} *M* Co^{2+}, and 10^{-3} *M* V^{2+}, approximately half of the OH radicals react with the Co^{2+} and half with the V^{2+} ions, in about 10^{-7} sec. The V^{3+} ions do not interfere, and the reaction between the newly formed Co^{3+} and the V^{2+} ions can be followed. Laurence et al. [6] have been studying reaction (4) in the presence of Cl^- ions in order to evaluate the effects of bridging ligands on the reaction and to determine whether the reaction is of inner or outer sphere type. The method has given results which are in agreement with those obtained from the competition stopped-flow studies. It is obvious that for systems of this kind it is important to know the effects of possible competing reactions.

The application of kinetic measurements can frequently lead to thermodynamic or even structural information about such short lived oxidation states. The application of the ionic strength dependence of the rate constant for reaction between charged reactants has of course been used to show that the charge on the hydrated electron is −1 and Laurence et al. [7] were able to show that the charge on the chloro-complex of Pt^{III} produced from $PtCl_6^{2-}$ is −1, suggesting that the structure is either $PtCl_4^-$ or perhaps $PtCl_3OH^-$.

Measurement of the rate constants for the forward and reverse paths for an equilibrium leads directly to the reduction potentials for the intermediate oxidation state and an example of a study of this kind is the determination of the reduction potentials for the couples involving Tl^{II} which is discussed below.

On radiolysis in aqueous solution, $Ni(CN)_4^{2-}$ is reduced to $Ni_2(CN)_6^{4-}$ by the radical ion CO_2^-. The proposed reaction mechanism is:

$$Ni(CN)_4^{2-} + CO_2^- \rightarrow Ni(CN)_4^{3-} + CO_2 \tag{5}$$
$$Ni(CN)_4^{3-} \rightarrow Ni(CN)_3^{2-} + CN^- \tag{6}$$
$$2\,Ni(CN)_3^{2-} \rightarrow Ni_2(CN)_6^{4-} \tag{7}$$

The yield of $Ni_2(CN)_6^{4-}$ is 2.4 molecules per 100 eV and the rate constants are:

$k_5 = (1.17 \pm 0.07)\ 10^9$ l mole^{-1} sec^{-1}
$k_6 = (8.1 \pm 1.0)\ 10^3$ sec^{-1}
$k_7 = (7.4 \pm 1.0)\ 10^7$ l mole^{-1} sec^{-1}

Spectra of the intermediate species have been recorded.

In the presence of methanol as a radical scavenger the yield of $Ni_2(CN)_6^{4-}$ is much lower and this is explained on the basis of a reaction between the $\cdot CH_2OH$ radical and $Ni_2(CN)_6^{4-}$ or its precursors. The following rate constants are reported. $k_{Ni(CN)_4^{2-}+H} = (1.8 \pm 0.2)\cdot 10^{10}$ l mole^{-1} sec^{-1} and $k_{Ni(CN)_4^{2-}+OH} = (9.1 \pm 0.5)\cdot 10^9$ l mole^{-1} sec^{-1}. The spectra of $HNi(CN)_4^{2-}$ and $Ni(CN)_4^-$ are given.

For the reaction between $Rh(bipyr)_3^{3+}$ ion and formate radical, CO_2^-, Mulazzani et al. [8] have found:

$Rh(bipyr)_3^{3+} + CO_2^- \rightarrow Rh(bipyr)_3^{2+} + CO_2$ and $k = (6.2 \pm 0.6) \cdot 10^9$ l mole^{-1} sec^{-1}.

For the reaction

$$Rh(bipyr)_3^{3+} + (CH_3)_2COH \rightarrow Rh(bipyr)_3^{2+} + ... \qquad (9)$$

$k = 2.9 \cdot 10^9$ l mole^{-1} sec^{-1}

and for the reaction

$$Rh(bipyr)_3^{3+} + e_{aq}^- \rightarrow Rh(bipyr)_3^{2+} \qquad (10)$$

$k = (5.9 \pm 0.6) \cdot 10^{10}$ l mole^{-1} sec^{-1}

Experiments are in progress on the pulse radiolysis of $Rh(bipyr)_3^{3+}$ ion in aqueous N_2O saturated solutions, i.e., for the reaction of the Rh ion with OH radicals.

$Os(NH_3)_5N_2^{2+}$ reacts with the OH radical with a rate constant of $1 \cdot 10^{10}$ l mole^{-1} sec^{-1} giving a species having an absorption maximum at 380 nm. This species is identified as $Os(NH_3)_4NH_2N_2^{2+}$, the product of the dehydrogenation of $Os(NH_3)_5N_2^{2+}$ by the OH radical.

For the thermal electron exchange reaction between Tl^{I} and Tl^{III}, an extensively studied oxidation—reduction reaction between metal ions in which a two-equivalent change is possible. Mechanisms in which the exchange occurs by a single two-electron transfer and by two one-electron transfers have been proposed but are still uncertain. The intermediate oxidation state, Tl^{II}, first observed as the product of the oxidation of Tl^{I} by OH radicals obtained by pulse radiolysis:

$$Tl^+ + OH \rightarrow TlOH^+ \qquad (11)$$

$$TlOH^+ + H^+ \rightarrow Tl^{2+} + H_2O \qquad (12)$$

has also been produced recently by flash photolysis [9].

$$TlOH^{2+} \rightarrow Tl^{2+} + OH \qquad (13)$$

and some interesting consequences have been obtained for the interpretation of a number of redox reactions of Tl^{I} and Tl^{III}, including the determination of the standard reduction potentials for the two couples:

$$Tl^{III} + e \rightarrow Tl^{II} \quad E_1^0 = +0.31 \text{ V} \qquad (14)$$

$$Tl^{II} + e \rightarrow Tl^{I} \quad E_2^0 = +2.22 \text{ V} \qquad (15)$$

and of the rate constants for the reactions of a number of transition metal aquo ions with Tl^{II} ions.

The most important reactions which have been measured are those between Tl^{II} and Fe^{III} or Co^{II}. From the value of E_2^0, Tl^{2+} appears to be a very powerful oxidising agent in acid solution. From E_1^0 and E_2^0 it is possible to calculate the potential of the Tl^{III}/Tl^{I} couple as +1.27 V, in agreement with the literature value of +1.25 V, and to comment on the mechanism of the electron-exchange reaction between Tl^{III} and Tl^{I}. The formation of Tl^{2+} ions is excluded and the data are in favour of a single two-electron transfer step.

The standard reduction potentials, E_1^0 and E_2^0, can be applied to a large number of oxidation—reduction reactions of Tl^I and Tl^{III} which are believed to involve the intermediate formation of Tl^{II}. It has been found that those reactions which proceed by a two-electron transfer process have a higher free energy of activation for a given ΔG^0 than those which proceed by one-electron transfer and are consequently slower. The data for the reactions between Tl^{2+} and $Ru(dipy)_3^{2+}$ and $Os(dipy)_3^{2+}$ are anomalous in that the apparent $\Delta G^{\ddagger}$ is lower than ΔG^0.

At the FRAE Lab. Laurence [10] very recently studied the reactions between Tl^{2+} and $Ru(dipy)_3^{2+}$ or $Ru(dipy)_3^{3+}$:

$$Tl^{2+} + Ru(dipy)_3^{2+} \rightarrow Tl^{+} + Ru(dipy)_3^{3+} \quad (16)$$
$$Tl^{2+} + Ru(dipy)_3^{3+} \rightarrow Tl^{3+} + Ru(dipy)_3^{2+} \quad (17)$$

which apparently proceed with almost the same rate constants and have also been assumed as pathways in the oxidation of $Ru(dipy)_3^{2+}$ by Tl^{3+}.

For the first reaction $k_{16} = 1.9 \pm 0.2 \cdot 10^9$ l mole^{-1} sec^{-1} was found, for the second $k_{17} = 7.5 \pm 0.2 \cdot 10^8$ l mole^{-1} sec^{-1}; the ratio of the rate constants for the Ru^{II} and the Ru^{III} complexes is in good agreement with the ratio deduced by Laurence and Balzani [6] from photosensitization experiments (1.5 and 1.6 respectively). Again there was no evidence of more than a single outer-sphere electron transfer step in the reaction, and the cause of the discrepancy between ΔG^0 and $\Delta G^{\ddagger}$ for the reaction between Tl^{3+} and $Ru(dipy)_3^{2+}$ must be found elsewhere.

Further reactions investigated quite recently are those of OH, Cl_2^- and Br_2^- with $Ru(dipy)_3^{2+}$. It is probable that rapid reactions interfere with that between Tl^{2+} and $Ru(dipy)_3^{2+}$. Ruthenium(II) complex reacts readily with OH and Cl_2^- radicals, but not with Br_2^-. The spectral changes suggest the formation of an intermediate species followed by a slower change to the final product which is not however $Ru(dipy)_3^{3+}$. It has the same spectrum as that observed after continuous irradiation with Linac electrons or with ^{60}Co gamma rays, and is a dark red solution, unlike the yellow Ru^{II} complex or the green Ru^{III} complex. The product cannot be reduced back to Ru^{II}, unlike $Ru(dipy)_3^{3+}$ and has not yet been identified. The much reduced extinction coefficient at 290 nm, which is due to the π—π^* transition in the dipyridyl ligands, suggests however that a loss of conjugation has taken place.

In connection with this Cl_2^- research, it may be recalled that the radical ions Cl_2^-, Br_2^-, I_2^-, $(SCN)_2^-$ have been invoked as reactive intermediates in redox reactions involving halogens or halide ions for many years. The reaction by which they are generated in the radiolysis of aqueous solutions of the halides is complex but the effect of the pulse is in many cases to produce them instantaneously.

$$X^- + OH \rightarrow XOH^- \quad (18)$$
$$XOH^- \rightarrow X + OH^- \quad (19)$$
$$XOH^- + X^- \rightarrow X_2^- + OH^- \quad (20)$$

$XOH^- + H^+ \rightarrow X + H_2O$ (21)
$X + X^- \rightarrow X_2^-$ (22)

The disproportionation reaction is:

$X_2^- + X_2^- \rightarrow X_3^- + X^-$ (23)

Laurence and Thorton [11] have recently studied reactions with the divalent metal ions of the first transition series from V^{2+} to Cu^{2+} using both flash photolysis and pulse radiolysis to generate the radical anions X_2^-:

$M^{2+} + X_2^- \rightarrow M(III) + 2\,X^-$ (24)

The radicals are particularly easy to determine because they have large extinction coefficients in the region at about 350 nm.

The reactions of the halogen radical ions X_2^- (X = Cl, Br, I, SCN) with metal ions are of interest because although the reduction of metal ions by ligands has been under investigation for some time, very few oxidations of metal ions by ligands or potential ligands are known. The factors effecting the electron transfer reactions can be varied over a wide range, for not only do the standard reduction potentials of the radical anions themselves differ by 1.3 V from Cl_2^- to I_2^-, but the standard reduction potentials of the metal ions vary from −0.4 V (Cr^{3+}) to +2.2 V (Cu^{3+}), so that the range of free energy covered is very large indeed. The substitution rates of the metal ions also cover a wide range, from 10^2 l mole^{-1} sec^{-1} for V_{aq}^{2+} to 10^9 l mole^{-1} sec^{-1} for Cr_{aq}^{2+} and Cu_{aq}^{2+}, and the effects of electronic configuration are also pronounced. The opportunity to measure the rate constants for reactions which have been postulated to occur in the reactions between halogens, halides and metal ions has enabled light to be shed on the mechanisms of some of these reactions. The radical anions can also undergo oxidation to the corresponding halogen. Only one such reaction has been measured so far, that between Fe^{3+} ions and I_2^- radical ions. Work is in progress on other oxidations, and in particular those of I_2^- ions.

CONCLUSION

This account has attempted to show that the application of pulse radiolysis to the study of coordination compound reactions can lead to novel and useful results, and that it is now possible to include pulse radiolysis among the techniques which can be used to define a reaction scheme or to test a mechanism.

The literature of coordination reaction mechanisms is littered with intermediates which have so far been inferred, and whose rates and mechanisms of reaction are only postulated. These postulated properties may often be wrong. Pulse radiolysis offers a useful and in many cases a unique tool for their investigation.

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