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Solvent-initiated photochemistry of transition metal complexes

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Contents

Abstract

Although it is generally assumed that photoreactions of transition metal complexes proceed through metal complex excited states, some reactions in halogenated solvents occur instead as radical processes, following carbon–halogen bond homolysis. Oxidation, substitution, or oxidative addition can occur by either a metal-centered or a solvent-initiated photoreaction, and they can be hard to distinguish. Under some circumstances even the kinetic rate laws can be the same. However, with proper choice of irradiation wavelength the dependence of the initial rate on light intensity and metal complex concentration suffices to discriminate between the two possibilities. © 1997 Elsevier Science S.A.

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1. Introduction

The paradigm in inorganic photochemistry consists of a transition metal complex that absorbs light, usually in the visible and UV, undergoes internal conversion and/or intersystem crossing, and reaches an excited state that can undergo chemical reaction and has a lifetime long enough to do so, often the lowest excited state of a given spin multiplicity [1–3]. The excited state complex may be able to make use

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of its additional electronic energy to undergo reactions not available to the ground state molecule, including oxidation, reduction, ligand substitution, or decomposition. Or it may transfer its energy to a substrate that can react further. Transition metal complexes, with a wealth of accessible d–d and charge transfer electronic states, and often several available oxidation states, are particularly well suited to this role.

Consider one such reaction, the photooxidation of hexakis(2,6-diisopropylphenylisocyano) complexes of Cr(0), Mo(0), and W(0), which was studied by Mann et al. [4]. Irradiation of these complexes in pyridine at 436 nm caused ligand substitution by pyridine. When irradiated in chloroform, a less nucleophilic solvent, $[M(CNIPh)_6]$ was oxidized to $[M(CNIPh)_6]^+$. In deaerated solutions the quantum yield was 0.19 for all three metals. The quantum yield was higher in air-saturated solutions, 0.70 for the Cr(0) complex. The authors proposed a mechanism based on reduction of chloroform by the excited state ML_6 complexes, and suggested that diffusion of the reduction product, $HCCl_3^{\cdot -}$, from the resulting ion pair is rate controlling, so that the equal quantum yields for the three metals might be explained.

In order for the three quantum yields to be equal when the rate of photoreduction by ML_6^* does not substantially exceed the rates of other deactivation processes, some rather special circumstances must apply. The enhanced quantum yield in aerated solutions is also problematical, since the effect of O_2 on photochemical reactions rates, when it has one, is usually to slow them down by quenching the excited state. The authors propose that the higher quantum yield "could reflect the increased diffusion rate of O_2^-," without further elaboration.

What is striking is not that these explanations are wrong; they may well be correct. It is that in the face of two rather unusual features for a photochemical system, no alternative to a metal-centered primary photoprocess was brought up, if only to refute.

The principle that photochemical reactions generally take place from the lowest excited state of a spin manifold is often termed Kasha's Rule, though Kasha's reference was to luminescence rather than photochemistry [5]. There are many examples of reactions in which it is violated [6], and the most common explanation for a violation is that the lowest excited state is unreactive. For example, a ligand field (LF) excited state may not participate in a redox reaction while a higher charge transfer to ligand (CTTL) state does.

When the solvent is also a substrate, it is often proposed that a charge transfer to solvent (CTTS) excited state is reactive, perhaps the only reactive excited state. CTTS states represent the promotion of an electron from the complex to an atom-like orbital defined by the potential from a cage of solvent molecules. The corresponding bands in the absorption spectrum are commonly in the UV, which can explain why visible irradiation may yield no reaction.

An alternative explanation for a reaction that occurs only under UV irradiation is that the bulk solvent is the photoactive species, but this possibility is rarely brought up in the literature of inorganic photochemistry. With halogenated solvents and some others, however, light absorption leads to bond homolysis, and several reactions are possible that mimic ordinary photoreactions in which the metal complex is photoactive.

$$\mathrm{RY} \xrightarrow{h\nu} \mathrm{R}^{\bullet} + \mathrm{Y}^{\bullet} \tag{1}$$

$$\mathrm{MX} + \mathrm{Y}^{\bullet} \rightarrow \mathrm{MY} + \mathrm{X}^{\bullet} \tag{2}$$

$$\mathrm{MX} + \mathrm{Y}^{\bullet} \rightarrow \mathrm{MX}^{+} + \mathrm{Y}^{-} \tag{3}$$

$$\mathrm{MX} + \mathrm{Y}^{\bullet} \rightarrow \mathrm{MXY} \tag{4}$$

Reactions (2) to (4) with a metal complex MX illustrate substitution, oxidation, and oxidative addition, any of which might have occurred through attack by an MX* excited state on the solvent. The metal-centered pathway may also generate radicals, so detection of radical intermediates or termination products is of limited utility in distinguishing a metal-centered from a solvent-initiated photoreaction.

The question has to do with the species that absorbs light to begin the primary photoprocess. It is either the bulk solvent or the metal complex, in whatever association with the solvent it may find itself. These alternatives can, in principle, be distinguished by the kinetic behavior of the reaction, that is, the rate law.

2. Kinetics

A "normal" photoreaction with a substrate, that is, one in which the metal complex is photoactive, can be represented as

$$\mathrm{A}^* + \mathrm{S} \xrightarrow{k_3} \mathrm{B} \tag{5}$$

If the rate constants for radiative and nonradiative deactivation are k_1 and k_2, and the rate of formation of the excited state is $I_0 f/V$, where I_0 is the incident light intensity and f the fraction of the incident light absorbed by MX, the rate law is, assuming a steady state concentration of [MX*],

$$\frac{\mathrm{d[B]}}{\mathrm{d}t} = k_3[A^*][\mathrm{S}] = \frac{I_0 f}{V} \cdot \frac{k_3[\mathrm{S}]}{k_1 + k_2 + k_3[\mathrm{S}]} \tag{6}$$

The last factor is the quantum yield, ϕ, for the process. The kinetic dependence derives from the fraction of light absorbed which, based on the total absorbance by solvent, reactant, and product, leads to the following equation under monochromatic irradiation (the path length is assumed to be 1.0 cm):

$$\frac{\mathrm{d[B]}}{\mathrm{d}t} = \frac{I_0}{V} \{1 - 10^{-(A_\mathrm{S} + \epsilon_\mathrm{A}[\mathrm{A}] + \epsilon_\mathrm{B}[\mathrm{B}])}\} \frac{\epsilon_\mathrm{A}[\mathrm{A}]\phi}{A_\mathrm{S} + \epsilon_\mathrm{A}[\mathrm{A}] + \epsilon_\mathrm{B}[\mathrm{B}]} \tag{7}$$

In Eq. (7), A_S is the solvent absorbance, and ϵ_A and ϵ_B are the extinction coefficients of reactant and product, all at the irradiation wavelength. The rate may also be expressed as

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t}=\frac{I_0}{V}\{1-10^{-(A_\mathrm{S}+\epsilon_\mathrm{B}C_0+(\epsilon_\mathrm{A}-\epsilon_\mathrm{B})[\mathrm{A}])}\}\frac{\epsilon_\mathrm{A}[\mathrm{A}]\phi}{A_\mathrm{S}+\epsilon_\mathrm{B}C_0+(\epsilon_\mathrm{A}-\epsilon_\mathrm{B})[\mathrm{A}]} \quad (8)$$

where C_0 is the initial concentration of the metal complex A.

Though the kinetic dependence on [A] is complex, Eq. (8) applies to every photoreaction of this type, and consequently experimental rate laws are almost never determined. It is a common observation, however, that photoreactions are zero order in the photoactive reactant for a significant fraction of the total reaction. This is usually a result of irradiation of an optically dense solution at a wavelength absorbed much more strongly by the reactant than the product. The exponential term is approximately zero (that is, $f\approx 1$) and the concentration of A cancels in numerator and denominator.

There are also circumstances under which behavior close to first order is expected. These include the following:

(1) Irradiation is near an isosbestic point; then $\epsilon_\mathrm{A}\approx\epsilon_\mathrm{B}$, and the total absorbance is approximately constant during the reaction.

(2) The total absorbance is small; then $1-10^{-(A_\mathrm{S}+\epsilon_\mathrm{A}[\mathrm{A}]+\epsilon_\mathrm{B}[\mathrm{B}])}\approx 2.3(A_\mathrm{S}+\epsilon_\mathrm{A}[\mathrm{A}]+\epsilon_\mathrm{B}[\mathrm{B}])$, and the rate is approximately $2.3I_0\epsilon_\mathrm{A}[\mathrm{A}]\phi/V$.

(3) $A_\mathrm{S}\gg\epsilon_\mathrm{A}[\mathrm{A}]+\epsilon_\mathrm{B}[\mathrm{B}]$, so that the rate is approximately $I_0\epsilon_\mathrm{A}[\mathrm{A}]\phi\cdot(1-10^{-A_\mathrm{S}})/A_\mathrm{S}V$.

For comparison, consider the following solvent-initiated photoreaction sequence:

$$\mathrm{RCl}\xrightarrow{h\nu,\,\phi_\mathrm{c}}\mathrm{R}^\bullet+\mathrm{Cl}^\bullet \quad (9)$$

$$\mathrm{Cl}^\bullet+\mathrm{A}\rightarrow\mathrm{B} \quad (10)$$

$$2\mathrm{R}^\bullet\rightarrow\mathrm{R}_2 \quad (11)$$

Reaction (10) may represent either electron transfer or oxidative addition to the metal complex A. Under steady state conditions the rate expression is

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t}=\frac{I_0}{V}\{1-10^{-(A_\mathrm{S}+\epsilon_\mathrm{A}[\mathrm{A}]+\epsilon_\mathrm{B}[\mathrm{B}])}\}\frac{A_\mathrm{S}\phi_\mathrm{c}}{A_\mathrm{S}+\epsilon_\mathrm{A}[\mathrm{A}]+\epsilon_\mathrm{B}[\mathrm{B}]} \quad (12)$$

This rate law can be readily distinguished from that of Eq. (7) for a metal-centered process. The choice of an irradiation wavelength that is only weakly absorbed, or one near an isosbestic point, will lead to zero-order kinetics rather than first-order. Irradiation of a strongly absorbing solution at a wavelength where $\epsilon_\mathrm{A}\gg\epsilon_\mathrm{B}$ will bring about a reaction order of minus one.

Non-chain radical processes are likely in solvents such as CCl_4, in which the number of possible propagation steps is limited. In protic halogenated solvents, hydrogen abstraction can cause propagation. The following sequence of steps represents a possible solvent-initiated chain process.

$$\mathrm{CHCl_3} \xrightarrow{h\nu,\,\phi_c} {}^{\bullet}\mathrm{CHCl_2} + \mathrm{Cl}^{\bullet} \tag{13}$$

$$\mathrm{Cl}^{\bullet} + \mathrm{CHCl_3} \xrightarrow{k_1} \mathrm{HCl} + {}^{\bullet}\mathrm{CCl_3} \tag{14}$$

$${}^{\bullet}\mathrm{CHCl_2} + \mathrm{CHCl_3} \xrightarrow{k_2} \mathrm{CH_2Cl_2} + {}^{\bullet}\mathrm{CCl_3} \tag{15}$$

$${}^{\bullet}\mathrm{CCl_3} + \mathrm{MX(\mathbf{A})} \xrightarrow{k_3} \mathrm{MCl(\mathbf{B})} + \mathrm{X}^{\bullet} + :\mathrm{CCl_2} \tag{16}$$

$$\mathrm{X}^{\bullet} + \mathrm{CHCl_3} \xrightarrow{k_4} \mathrm{HX} + {}^{\bullet}\mathrm{CCl_3} \tag{17}$$

$$2{}^{\bullet}\mathrm{CCl_3} \overset{k_5}{\rightarrow} \mathrm{C_2Cl_6} \tag{18}$$

This unbranched chain mechanism leads under steady state conditions to the rate law

$$\frac{\mathrm{d[B]}}{\mathrm{d}t} = \frac{I_0^{1/2}}{V^{1/2}} \{1 - 10^{-(A_\mathrm{S} + \epsilon_\mathrm{A}[\mathrm{A}] + \epsilon_\mathrm{B}[\mathrm{B}])}\}^{1/2} \frac{A_\mathrm{S}^{1/2} \phi_\mathrm{c} [\mathrm{A}]}{k_5^{1/2} \{A_\mathrm{S} + \epsilon_\mathrm{A}[\mathrm{A}] + \epsilon_\mathrm{B}[\mathrm{B}]\}^{1/2}} \tag{19}$$

In spite of the square roots in this expression, it is easily possible to mistake a solvent-initiated reaction governed by Eq. (19) for a metal-centered reaction obeying Eq. (7). This is especially true under the conditions leading to approximate first-order behavior, all of which apply just as well to Eq. (19). A highly absorbing solution with $\epsilon_\mathrm{A} \gg \epsilon_\mathrm{B}$, which is zero order under Eq. (7), would be half order under Eq. (19). Thus, careful design of the reaction conditions may enable the two mechanisms to be distinguished in the course of one kinetic run.

Three other methods are probably more reliable in distinguishing metal-centered from solvent-initiated chain reactions.

(1) The square root dependence on light intensity in Eq. (19) is quite unambiguous. Furthermore, many other chain mechanisms with bimolecular termination steps will also exhibit the same square root dependence.

(2) The wavelength dependence will also readily distinguish the two types of mechanism, once the common factor of the total fraction of light absorbed divided by the total absorbance is accounted for. The metal-centered reaction tracks the absorption spectrum of the metal complex and the solvent-initiated reaction tracks the spectrum of the solvent.

(3) A third criterion by which solvent-initiated and metal-centered photoreactions may be distinguished is the variation of initial reaction rate with the starting concentration of metal complex ($[\mathrm{A}] = C_0$ and $[\mathrm{B}] = 0$ in Eqs. (7), (12) and (19)). For a metal-centered reaction (Eq. (7)) the initial rate will increase with increasing C_0 in dilute solution and will not change with C_0 in a strongly absorbing solution. Any

other behavior may be an indication that the reaction is not metal-centered. For the simple solvent-initiated reaction modeled by Eq. (12), the initial rate will not change with C_0 in dilute solution, but should vary inversely with C_0 in more concentrated solutions. Eq. (19) for a solvent-initiated chain reaction predicts that the initial rate will increase with increasing C_0 both in dilute and in optically dense solutions.

3. Solvent-initiated photoreactions

Though initiation by solvent absorption is seldom considered in inorganic photoreactions, reactions of radicals from the solvent with metal complexes do appear in the literature, for example [7],

$$\mathrm{CCl_3OO\cdot + Zn(TPP) \xrightarrow[CCl_4]{} CCl_3OO^- + Zn(TPP)^+} \tag{20}$$

(TPP = tetraphenylporphyrin). The trichloromethylhydroperoxy radical was formed from trichloromethyl radicals generated by pulse radiolysis rather than UV irradiation, and the metal might be considered incidental in the reaction, but it is nevertheless the type of process shown in Eq. (3).

The reaction

$$\mathrm{[Ru(bpy)_2(N_3)_2] \xrightarrow[CHCl_3]{h\nu} [Ru(bpy)_2Cl_2]} \tag{21}$$

(bpy = 2,2′-bipyridine) shows some characteristics of a solvent-initiated reaction [8,9]. Irradiation at 546 or 436 nm of $[\mathrm{Ru(bpy)_2(N_3)_2}]$ caused no reaction, even though absorbed strongly, and even though the excited states are quite similar to the CTTL excited states of $[\mathrm{Ru(bpy)_3}]^{2+}$ that are so reactive [10]. The reaction was interpreted as a solvent-initiated process like Eq. (2). In a solution of moderate optical density, the kinetic dependence on the starting complex was first order. Since the reactant and product have similar extinction coefficients at the irradiation wavelength, however, a metal-centered photoreaction would show similar behavior. The variation of rate with light intensity and with starting concentration was not reported, and consequently the characterization of reaction 21 as solvent-initiated cannot be regarded as firmly established. There is some evidence, however, that the reaction rate follows the chloroform absorbance rather than that of $[\mathrm{Ru(bpy)_2(N_3)_2}]$ [9].

The reaction

$$\mathrm{[Ru(bpy)_2Cl_2] \xrightarrow[CHCl_3]{h\nu} [Ru(bpy)_2Cl_2]^+} \tag{22}$$

in aerated solution is more firmly established as solvent-initiated [11]. No reaction takes place in deaerated solution. No reaction occurs under 436 or 546 nm irradiation. The reaction rate is proportional to the square root of the light intensity, providing strong evidence that the solvent is photoactive. The experimental rate law can be rendered as

$$\frac{d[\mathrm{Ru(III)}]}{dt} = I_0^{1/2} f^{1/2} (c_1[\mathrm{Ru(II)}]^{1/2} + c_2) \qquad (23)$$

(f=fraction of light absorbed by chloroform). Fig. 1 is a plot of the rate data, in a somewhat different form than in the original [11]. The square root dependence on the concentration of [$\mathrm{Ru(bpy)_2Cl_2}$] shows that the mechanism is more complicated than that culminating in Eq. (19) above. The proposed mechanism includes the following steps:

$$^{\bullet}\mathrm{CCl_3} + \mathrm{O_2} \rightarrow \mathrm{CCl_3OO^{\bullet}} \qquad (24)$$

$$\mathrm{CCl_3OO^{\bullet}} + \mathrm{Ru(II)} \rightarrow \mathrm{Ru(III)} + \mathrm{CCl_3OO^-} \qquad (25)$$

$$\mathrm{CCl_3OOH} + \mathrm{Ru(II)} \rightarrow \mathrm{Ru(III)} + \mathrm{CCl_3O^-} + {}^{\bullet}\mathrm{OH} \qquad (26)$$

$$^{\bullet}\mathrm{OH} + \mathrm{CHCl_3} \rightarrow \mathrm{H_2O^{\bullet}} + \mathrm{CCl_3} \qquad (27)$$

It is proposed that [$\mathrm{Ru(bpy)_2Cl_2}$] is oxidized once by the peroxy radical through electron transfer and again by the hydroperoxide, through O–O bond cleavage. The latter process generates a chain-carrying radical. The termination process is complex and must explain both the dependence on $[\mathrm{Ru(II)}]^{1/2}$ and the nonzero intercept in Fig. 1 and Eq. (23) [11].

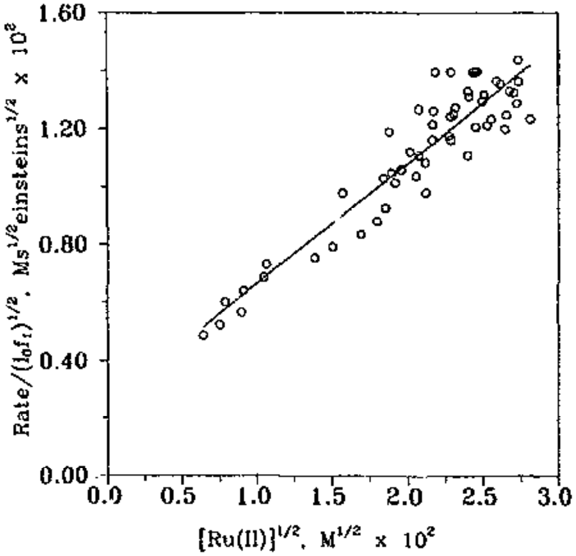

Fig. 1. Plot of kinetic data at different illumination intensities and concentrations, testing the empirical rate law, $(I_0 f)^{1/2}(c_1[\mathrm{Ru}]^{1/2} + c_2)$, where f is the fraction of light absorbed by chloroform.

4. Bidirectional photochemistry

The existence of a solvent-initiated process does not preclude a metal-centered photoreaction in the same system. The metal-centered reaction may occur in the same direction as the solvent-initiated process or in the opposite direction. The $[Ru(bpy)_2Cl_2]^{0/+}$ system in chloroform provides an example of the latter [8,11,12]. Excited $[Ru(bpy)_2Cl_2]$ can oxidize chloride ion; however, the lifetime of the excited state is so short that it can only react with ion-paired Cl^-.

$$\{[Ru(bpy)_2Cl_2]^+,Cl^-\} \xrightarrow{h\nu} [Ru(bpy)_2Cl_2]+Cl^{\cdot} \tag{28}$$

Both the solvent-initiated oxidation of Ru(II) and the metal-centered reduction of Ru(III) occur simultaneously under irradiation. This differs from classical bidirectional photochemistry, such as cis–trans isomerization reactions, in that a net reaction occurs with each cycle. In this case that reaction is the oxidation of $CHCl_3$ to CO_2 and HCl. The process is therefore photocatalytic.

Another interesting feature of the $[Ru(bpy)_2Cl_2]^{0/+}$ system in chlorinated solvents is a pronounced hypersensitivity of the Ru(II) and Ru(III) concentrations to temperature [12]. In air-saturated $CHCl_3$ under irradiation at 313 nm or below, the solution is virtually 100% Ru(II) at 60°C and below, and is virtually 100% Ru(II) at 60°C and above. At 59° a mixture of the two exists. A photostationary mixture can be achieved near 59°C if the solution is irradiated at a wavelength absorbed much more strongly by Ru(III) than Ru(II) (313 nm is one such wavelength). Then the concentrations adjust so that heating through light absorption by Ru(III), and some by Ru(II), balances cooling by the environment [12].

The 59°C transition temperature in chloroform is very near the boiling point (61°C), and the reason for the concentration reversal is that O_2, whose concentration is normally much in excess, is driven out by solvent vapor. There are other solvents and solvent systems, however, in which the Ru(II)/Ru(III) transition occurs at a temperature far from the boiling point, and a more complicated process must be involved.

5. Conclusions

Solvent-initiated photoreactions can mimic metal-centered photoreactions, and the two can be difficult to distinguish. Even the kinetic behavior during a particular reaction may be insufficient. When the photoreaction of a metal complex is with a solvent capable of bond homolysis, an explanation in terms of a metal complex excited state, even a charge transfer to solvent excited state, should not be made without first excluding the solvent-initiated alternative. This can frequently be done by examining the behavior of the initial rate with light intensity, starting concentration of the metal complex, and irradiation wavelength. A complete analysis will take into account the full rate law.

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