Viscosity and Concentration Effects on Charge Transfer Photochemistry. Tris(dibenzyldithiocarbamato)iron(III)

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Abstract: The changes of the rates and quantum yields of the charge transfer photochemical reaction of the title compound with halogenated hydrocarbons caused by changing the type of entering ligand, the concentration of the entering ligand, the viscosity of the medium, and the coordinating ability of the medium are quantitatively treated. One of the theoretical treatments used here was originally developed by Noyes for the scavenging of solvent caged radical pairs. The other treatment is based on a conventional kinetic analysis of competing reactions. Both treatments are applicable to the photoreactions of the title compound. The relative rates of the forward reaction (which produces the photoproducts) and the recombination reaction (which produces the starting material) are determined from the concentration dependencies of the observed quantum yield. The variations in the observed quantum yields with variations of the entering ligand are caused by changes in the rate of the forward reaction. For the most efficient entering ligands, the forward reaction is diffusion controlled. Its viscosity dependence follows the Debye theory and the observed quantum yields are proportional to the square root of the reciprocal of the viscosity. The recombination reaction is not diffusion controlled but is viscosity dependent. The competition of strongly coordinating solvents with the entering ligands is treated by the two theories.

The most common type of photoreaction of transition metal complexes in condensed media is reaction with the solvent or a solute.[1] In the case of ligand field photochemistry, recent models have suggested that excited state bond weakenings are responsible for the photoreactivity.[1-4] The bond weakenings may cause ligand dissociation followed by the new ligand entering the vacant coordination site (a "dissociative" mechanism) or it may cause weakening without dissociation followed by entering ligand attack at the site of the weakened metal-ligand bond (an "associative" mechanism). In the cases of charge transfer photochemistry, where the photoactive state involves metal to ligand or ligand to metal electron transfer, the mechanism may involve bond weakenings as above, changes in the metal oxidation state with concomitant ligand lability, and/or radical pair formation. Models to explain charge transfer excited state photochemistry have used molecular orbital theory,[5,6] and thermodynamic considerations.[7,8]

All of the above reactions can be profoundly affected by the medium. A general mechanistic scheme which will form the basis for quantitative treatment of the medium effects is represented by eq 1. A reactive intermediate, [M- -L], is formed

$$\begin{tikzcd} M{-}L \arrow[r, shift left, "I_a\Phi_0"] & {[M\text{-}\text{-}L]} \arrow[l, shift left, "k_1"] \arrow[r, "k_2", "RX"'] & {[MLRX]} \arrow[r, "k_p"] \arrow[ll, bend left, "k_b"] & MX + LR \end{tikzcd} \qquad (1)$$

with a quantum yield Φ_0 from the original metal complex M-L. The reactive intermediate can undergo deactivation with rate constant k_1. Competing with deactivation is a reaction with a solvent or solute molecule, RX, to produce a complex with rate constant k_2. (In the system to be discussed here, k_2 is second order.) The complex forms the photoproduct with rate constant k_p, or undergoes a back-reaction to produce the starting material with rate constant k_b. In the case of a dissociative reaction, [M- -L] would have a reduced coordination number and the complex is the product (i.e., $k_p = k_b = 0$). For an associative reaction, the complex would have an expanded coordination sphere and k_p and k_b represent loss of the original ligand and the newly entered ligand, respectively. The quantum yield Φ_0 includes all of the internal energy processes in the original metal complex including internal conversion, nonreactive radiationless transitions to the ground state, and luminescence. The value of Φ_0 could be dependent on the medium although it is likely that the primary internal energy processes are less medium dependent than the rate constants in eq 1. The reactive intermediate could be a thermally equilibrated excited state, solvent caged dissociative fragments, or radical pairs. The overall observed quantum yield represents the results of the competition between the reactions leading to the product and the back and deactivation reactions giving the starting material. Several of the above processes collectively contribute to what is called the "cage effect".[9,10]

The electronic models which have been developed to explain the photoreactivity of transition metal complexes deal with some of the internal aspects of the electronic processes which are related to the quantum yield of formation of the reactive intermediate, (i.e., the quantity Φ_0 in eq 1), and perhaps reflect those aspects of the rate of the product producing reaction (k_2 in eq 1) which are governed by the bond weakenings of the excited complex. The models do not treat the reactions, k_1 and k_b, nor do they include those aspects of the product producing reaction which are governed by the entering ligand itself. In short, the models may be applicable to similar complexes under identical conditions of the medium, but they do not include the effects of varying the medium. This latter aspect is the subject of this paper.

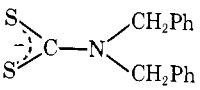
Two properties of the medium which potentially can be the most helpful in probing the quantitative details of the medium effects on the photoreactivity are the viscosity of the solution[10-13] and the reactivities of the entering ligand toward the metal.[1,14] In order to quantitatively study the above effects, the transition metal complex should possess the following properties: good solubility in a wide variety of polar and nonpolar solvents, a strong dependence on the nature and concentration of the entering ligand, and a large reaction quantum yield.

A complex which possesses all of the above properties is tris(dibenzyldithiocarbomato)iron(III). Because it is soluble in nonpolar solvents, the viscosity can be varied by using long chain hydrocarbons without appreciably changing the polarity or coordinating ability of the medium. In addition, because the complex and the photoproduct are uncharged, complications arising from ion-pairing are avoided. The photochemical reaction is strongly dependent on the nature of the reacting ligand with quantum yields varying over several orders of magnitude depending on which entering ligand is used.[15,16] The complex is highly photoactive with the maximum quantum yield of product formation approaching 1.0.

The free radical nature of the reaction has been well characterized[15,16] and is shown in eq 2. The reactive intermediate

$$\mathrm{Fe^{III}(DTC)_3} \overset{h\nu}{\rightleftharpoons} [\mathrm{Fe^{II}(DTC)_2 \cdot DTC}] \xrightarrow[\mathrm{[RX]}]{} \mathrm{Fe(DTC)_2X} + (\mathrm{DTC\text{-}R}) \quad (2)$$

DTC =



is a formal iron(II) complex which abstracts halogen radicals from halogenated hydrocarbons, hereafter called RX. The observed quantum yield depends on the carbon–halogen bond strength. When RX = $CHCl_3$ or CCl_4, the quantum yields in the neat solvents are 0.048 and 0.10, respectively.[15] When the concentrations of these RX reactants are lower than 10^{-1} M, no reaction is observed. When RX = CBr_4, the quantum yield is 0.87 at RX = 2.39×10^{-1} M. The quantum yield decreases with decreasing CBr_4 concentration and is still measurable at $[CBr_4] = 2 \times 10^{-5}$ M. Concentrations of CBr_4 greater than 2.4×10^{-1} M cannot be used because of the onset of a competing thermal reaction. This paper reports the quantitative aspects of the entering ligand and medium dependence of the quantum yield for $Fe(DTC)_3$.

Experimental Section

Compounds. $Fe(Bz_2DTC)_3$ was prepared by the literature method.[17] Anal. Calcd for $C_{45}H_{42}N_3S_6Fe$: C, 61.90; H, 4.86. Found: C, 62.10; H, 4.70.

Carbon tetrabromide (Matheson Coleman and Bell) was recrystallized twice to give colorless crystals before use.

The benzene (thiophene free, analytical reagent grade, Mallinckrodt), hexane (spectroquality, Matheson Coleman and Bell), carbon tetrachloride (spectrophotometric grade, Mallinckrodt), chloroform (analytical reagent grade, Mallinckrodt), and hexadecane (99%, olefin free, Matheson Coleman and Bell) were freshly redistilled before use. Nujol was purchased from Plough, Inc.

Instrumentation. The electronic absorption spectra and the absorbance changes for quantum yield measurements were taken using a Cary 14 spectrometer.

All of the relative photochemical rate studies were carried out using a Hanovia 450-W quartz Hg-vapor lamp operated at 100 W and a merry-go-round in the water bath thermostated at room temperature. Two layers of Pyrex glass cylinders (3.5 and 2.75 in. in diameter, absorbance > 1 at $\lambda \leq 305$ nm) were placed around the quartz lamp holder to filter out the high energy UV radiation. No additional filters were used to ensure maximum intensity in the photoactive bands between 320 and 360 nm.

Quantum Yield Studies. The quantum yields of the photoredox halogen abstraction reaction were obtained using the merry-go-round apparatus. The formation of the photoproduct, $Fe(Bz_2DTC)_2X$ ($X^- = Cl^-$ or Br^-), was measured by monitoring the increase in the absorbance at 615 and 630 nm, respectively. The actinometer was a 2.4×10^{-4} M solution of $Fe(Bz_2DTC)_3$ in chloroform (quantum yield = 0.048 ± 0.005).[15] All quantum yields were corrected for competing thermal reactions using a control solution maintained at the same temperature in the dark. Except for the runs at high CBr_4 concentrations, the thermal correction was less than 1%.

For the concentration dependence studies, benzene solutions of 2.4×10^{-4} M $Fe(Bz_2DTC)_3$ with various halogenated hydrocarbon concentrations were prepared. The concentration of RX ranged from 1 to 12 M for chloroform and carbon tetrachloride and from 2×10^{-5} to 10^{-3} M for carbon tetrabromide. Similar processes were followed for the studies in other supporting solvents such as acetonitrile, Me_2SO, and pyridine.

For the viscosity dependence study, the procedures described previously were followed except that the solutions were mixtures of benzene with viscous hydrocarbons (hexane, hexadecane, and Nujol) and RX ($CHCl_3$, CCl_4, CBr_4) in ratios appropriate to give the desired viscosity. The concentration of $Fe(Bz_2DTC)_3$ was kept at 2.4×10^{-4} in all solutions.

The room temperature viscosity of each solution was measured using an Ostward viscometer.[18]

Theory

Two treatments of the reactions shown in eq 1 will be discussed in this paper: the Noyes theory,[19-21] and conventional kinetic theory. The Noyes theory was originally developed to treat the scavenging of photo-produced radical pairs in solution.[19-21] In particular, it was designed to treat the case of scavenging which competes with the secondary recombination of the radical pairs, a case in which the time dependence of the recombination should prevent a classical kinetic treatment from being valid.[19] On the other hand, the kinetic treatment uses the conventional rate constants for all processes including the recombination reaction. The symbols, units, and assumptions of both theories will be outlined in this section.

In the Noyes model, the photolytically produced radical fragments undergo three processes: primary recombination in the solvent cage, secondary recombination after diffusive displacements on the order of a molecular diameter, and a total escape from each other.[19] Because the probability that the fragments will undergo secondary recombinations varies inversely as $t^{3/2}$, conventional kinetic treatments should not be applicable to these processes.[19-20] The expression derived by Noyes is given in eq 3 where γ_{obsd} is the observed quantum yield, a is a constant related to secondary recombination, k_s is the rate constant for production of products, γ_r is the quantum yield in the presence of the scavenger at concentrations which are sufficient to prevent radical recombination in the bulk but too low to compete with secondary recombination, and Γ is the quantum yield for radicals escaping primary recombination.

$$\gamma_{\mathrm{obsd}} = \gamma_r + 2a\Gamma(\pi k_s[\mathrm{RX}])^{1/2} \quad (3)$$

The maximum values of a and k_s estimated by Noyes are about 10^{-6} $s^{1/2}$ and 10^{10} L/(mol s), respectively.[19]

In the conventional kinetic treatment of the photoreaction in eq 1, the steady state approximation is applied to the reactive intermediate. The rate of the forward reaction producing the reactive intermediate is $I_a\Phi_0/NV$, where I_a is the number of photons absorbed by the starting metal complex in photons/s. Φ_0 is the quantum yield of production of the reactive intermediate in molecules/photon, N is Avogadro's number, and V is the volume of the solution in liters. The expression of most utility, obtained after applying the steady state approximation and rearranging, is

$$\frac{1}{\Phi_{\mathrm{obsd}}} = \frac{1}{\Phi_0}\left(\frac{k_p + k_b}{k_p}\right)\left(1 + \frac{k_1}{k_2[\mathrm{RX}]}\right) \quad (4)$$

In a plot of reciprocal rate vs. reciprocal RX concentration, the intercept, $(1/\Phi_0)((k_p + k_b)/k_p)$ contains information concerning the quantum yield of formation of the reactive intermediate. The slope, $(1/\Phi_0)((k_p + k_b)/k_p)k_1/k_2$, gives the ratio of the deactivation and forward rate constants.

Results

The results of treating the concentration dependence of the halogen abstraction photoreaction according to the Noyes theory are shown in Figure 1. Figure 1a shows the dependence of the observed quantum yield on the concentration of CBr_4 in supporting solvents which are noncoordinating (benzene) and coordinating (acetonitrile). Figure 1b shows the results for $CHCl_3$ at four orders of magnitude larger concentration. The results of varying the concentration of the coordinating solvent acetonitrile on the quantum yield (at constant CBr_4 concentration) are shown in Figure 1c. In all cases, the linear behavior expected from the Noyes theory is observed, but the intercepts are unexpectedly on the positive concentration axis. The slopes and intercepts of all of the studies are tabulated in Table I.

The effects of viscosity on the quantum yields are shown in Figure 2. The reaction with CBr_4 at low concentrations was highly viscosity dependent, while the reactions with CCl_4 and $CHCl_3$ at higher concentrations were viscosity independent

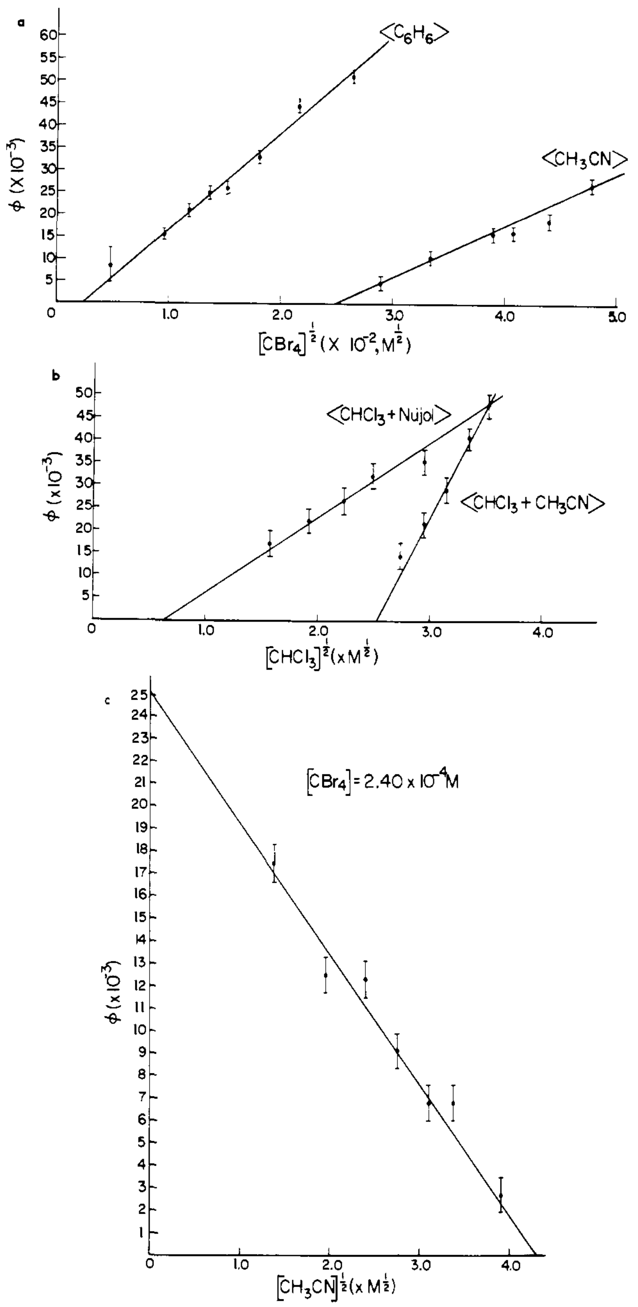


Figure 1. Noyes plots of the concentration dependence of the halogen abstraction reaction varying (a) CBr_4 in C_6H_6 and CH_3CN, (b) $CHCl_3$ in Nujol and CH_3CN, and (c) CH_3CN in benzene.

Table I. Slopes and Intercepts from the Noyes Plots of the Concentration Dependence of the Quantum Yields

Reactant	Supporting solvent	Slope, ($M^{-1/2}$)	(Intercept)^2, M
$CHCl_3$	C_6H_6	1.89×10^{-2}	6.64×10^{-1}
CCl_4	C_6H_6	4.05×10^{-2}	1.94×10^{-1}
CBr_4	C_6H_6	2.140	1.02×10^{-5}
CH_3CN	C_6H_6	5.83×10^{-3}	18.15 M
$CHCl_3$	CH_3CN	4.22×10^{-2}	5.68 M
CBr_4	CH_3CN	1.169	6.25×10^{-4}

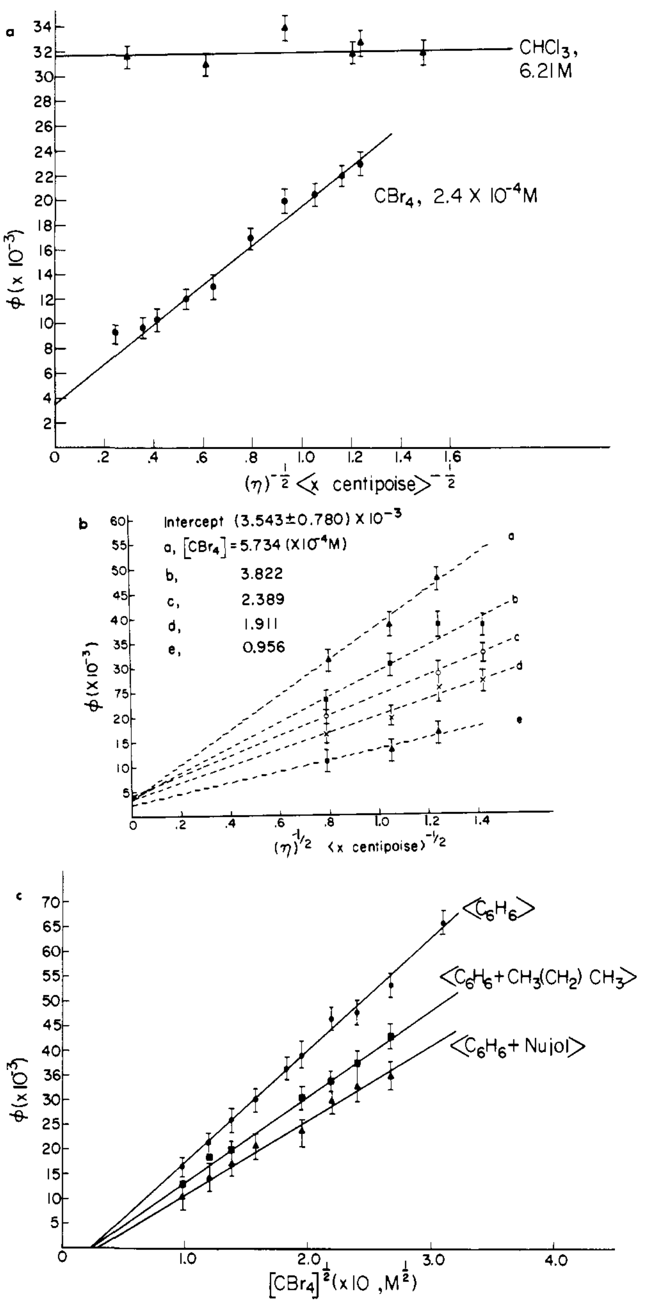


Figure 2. Viscosity effects. (a) Viscosity dependence of the reaction with CBr_4 and independence with $CHCl_3$. (b) Viscosity dependences of the reaction at various fixed CBr_4 concentrations. The dotted lines are least-squares fits to the data points. (c) Concentration dependence of the reaction at three viscosities.

as shown in Figure 2a. For the viscosity dependent reactions, plots of the quantum yield vs. the reciprocal square root of the viscosity were linear over the ranges of viscosities and CBr_4 concentrations shown in Figure 2b. The intercepts in these plots were constant on the positive quantum yield axis. The intercepts of the concentration plots in solutions of widely different viscosities were constant on the positive concentration axis as shown in Figure 2c. The slopes of the plots in Figures 2b and 2c, together with some relationships which will be discussed later are given in Tables II and III, respectively.

The results of treating the CBr_4 concentration dependence of the quantum yield according to kinetic theory are shown in Figure 3 for supporting media of two different viscosities. The plots of reciprocal quantum yield vs. reciprocal CBr_4 concentration are linear with intercepts independent of the viscosity.

Discussion

1. Viscosity and Concentration Dependence According to the Noyes Theory. According to the Noyes theory a plot of the quantum yield of the reaction vs. the square root of the entering ligand concentration will give a straight line with a slope of

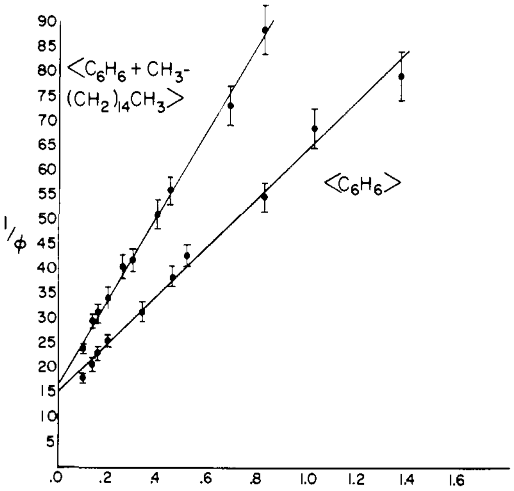


Figure 3. Kinetic treatment of the concentration dependences of the reaction at two different viscosities.

$2a\Gamma(\pi k_s)^{1/2}$ and an intercept of γ_r. If the rate constant for the production of products, k_s, is diffusion controlled, its value is given by the modified Debye equation,[22] eq 5, where η is the viscosity of solvent in centipoise units and d_1 and d_2 are the diameters of the reacting species which are assumed spherical.[22] For a given metal complex and entering ligand, k_s is inversely proportional to the viscosity. Thus, in the Noyes model, a plot of the quantum yield of the reaction vs. the square root of the reciprocal of the viscosity should also give a straight line when the reaction is diffusion controlled. If only the viscosity of the supporting medium is changed, the relative slopes of the lines should be proportional to $(\eta)^{-1/2}$. All of the above conditions are met for the photoreaction of $Fe(DTC)_3$ with halogenated hydrocarbons as shown in Figures 1 and 2. Therefore k_s is in the diffusion controlled limit.

$$k_s = \frac{1}{4}\left(2 + \frac{d_1}{d_2} + \frac{d_2}{d_1}\right)\frac{8RT}{10^5\eta} \tag{5}$$

The slopes of the plots are directly related to three independent parameters, a, Γ, and k_s.[21] It is impossible to solve for any one of these directly. However, under certain conditions such as are found when RX = CBr_4, an approximation is possible. By definition, the quantum yield for radical pairs which have escaped primary recombination, Γ, must be greater than the highest observed quantum yield of product formation directly measured in the experiment, 0.87. The exact proportionality of the slopes to the measured values of $(\eta)^{-1/2}$ in the viscosity plots, Figures 2a and 2b, indicates the k_s is diffusion controlled. The value of k_s in benzene solution is 1×10^{10} L/(mol s).[23] The slope of the plot of quantum yield vs. $[CBr_4]^{1/2}$ in benzene is 2.140 $mol^{1/2}/(L^{1/2}\ s)$. Thus the value of a must be $6.8 \times 10^{-6}\ s^{1/2}$. This value of a is of the same order of magnitude as the maximum value which has been estimated by Noyes.[19] The above calculation of a is not ambiguous for the CBr_4 reactions because the maximum values of k_s and Γ must be used.

In the case of the reactions with the chlorinated hydrocarbons CCl_4 and $CHCl_3$, the reactivity is lower than that observed with CBr_4 and the maximum values of the constants are not found. Thus, the decreased quantum yield may result because of changes in Γ and/or a as well as from changes in k_s. Because the observed quantum yields correlate well with the carbon-halogen bond strengths, the decreased reactivity is probably attributable to decreased values of k_s and not to indirect effects of RX on a or Γ.

In the plots of quantum yield vs. $(\eta)^{-1/2}$, Figures 2a and 2b, the intercepts in all cases gave $\gamma_r = 0.0035 \pm 0.0008$. According to the Noyes interpretation, this quantum yield represents the production of fragments from the photolyzed metal complex which escape recombination. The validity of this interpretation can be tested by measuring the quantum yield of decomposition of the complex in a neat supporting solvent in the total absence of entering ligand RX. The measured decomposition quantum yield under these conditions was 0.002 ± 0.0004, verifying the interpretation of the intercept.

Table II. Viscosity Dependence of the Quantum Yield as a Function of Scavenger Concentration (See also Figure 2b)

10^{-4} [RX], M	Slope ($cP^{-1/2}$)	S/S′	$([RX]/[RX]')^{1/2}$
5.734	3.63 ± 0.06		
3.822	2.66 ± 0.10	1.36 ± 0.07	1.22
2.389	2.01 ± 0.05	1.32 ± 0.08	1.26
1.911	1.83 ± 0.03	1.10 ± 0.05	1.12
0.956	1.13 ± 0.05	1.60 ± 0.11	1.41

Table III. Concentration Dependence of the Quantum Yields as a Function of Viscosity (see also Figure 2c)

Solvent	Viscosity η(cP)	Slope ($M^{-1/2}$)	ΦH S/S^{solv}	$(\eta^{sol}/\eta\Phi H)^{1/2}$
ΦH	0.658 ± 0.018	2.31 ± 0.04		
ΦH + hexadecane	0.898 ± 0.020	1.81 ± 0.09	1.28 ± 0.09	1.17
ΦH + Nujol	1.606 ± 0.078	1.54 ± 0.07	1.51 ± 0.10	1.56

The intercepts of the plots of quantum yield vs. $[RX]^{1/2}$ give a negative γ_r and a positive [RX] as shown in Figures 1a, 1b, and 2c contrary to the predictions of the Noyes model. The intercepts on the concentration axis varied with the nature of RX giving values of 1×10^{-5}, 2×10^{-1}, and 5×10^{-1} M for CBr_4, CCl_4, and $CHCl_3$, respectively. For a given RX in noncoordinating supporting solvents such as benzene and viscous hydrocarbons, the intercept was constant within experimental error. In coordinating solvents, the intercept drastically increased. The quantum yield for production of the five-coordinate photoproduct at zero scavenger concentration is zero. Thus, the plot is not linear at very low scavenger concentrations. Because the slope of the Noyes plot and the parameters derived from it appear to be meaningful at high scavenger concentrations, we interpret the intercept of the linear portion to represent the minimum RX concentration at which the scavenging dynamics represented by the Noyes theory are operative. At lower concentrations, different mechanisms or minor competing pathways may become important and cause the line to curve up toward zero. Three observations support this interpretation. When the RX concentration is large enough to be in the linear region, the Noyes plots of quantum yield vs. reciprocal square root viscosity give positive intercepts with a constant value equal to that of the residual quantum yield determined independently. Secondly, if the intercept does represent the minimum concentration necessary for the scavenging mechanism to be operative, its value should be consistent with the kinetic treatment, eq 4. Substituting the concentrations obtained from the square of the intercept into eq 4 and using the calculated values of the rate constants, the calculated quantum yields are consistent with the minimum quantum yields which can be observed. Finally, our interpretation is consistent with the known trends of the quantum yield and RX bond strength.[15] The larger the RX bond strength, the smaller the quantum yield and the larger the intercept, i.e., the higher the minimum concentration of the RX needed for the scavenging reaction.

2. Viscosity and Concentration Dependence Treated by Conventional Kinectic Theory. According to the kinetic treatment, a plot of the reciprocal of the rate of the product quantum yield vs. the reciprocal of the concentration of the entering group will give a straight line with a slope of $(1/\Phi_0)((k_p + k_b)/k_p)(k_1/k_2)$ and an intercept of $(1/\Phi_0)((k_p + k_b)/k_p)$. Such behavior is observed for the photoreaction under discussion. As expected from the bond energies of the halogenated hydrocarbons,[24] the ratios of k_1/k_2 decrease with decreasing carbon-halogen bond strength and are 15.9, 9.5, and 4.10^{-4} for $CHCl_3$, CCl_4, and CBr_4, respectively.

Because the slope depends on both the forward (k_2) and the deactivation (k_1) rate constants, the effect of viscosity on the slope is difficult to predict. If only k_2 depended on the viscosity, the relative values of the slopes in media of different viscosities would be proportional to the viscosities. If both k_2 and k_1 depended on the viscosity in the same manner, the slopes would be independent of the viscosity. If k_2 and k_1 were both viscosity dependent but with different functional forms, no simple relation would hold between the relative values of the slopes and the viscosities. The latter case is true for our system. If k_2 can be normalized for viscosity changes using the same functional form found from the variation of k_s, k_1 is calculated to be viscosity dependent but does not have the reciprocal square root dependence found for k_s. The different functional form could occur because the recombination reaction does not involve diffusion through the solvent but instead involves rotations and vibrations within the solvent cage. Alternatively, it could depend on the coupling of the excited state with the solvent (e.g., via solvent vibrations).

Because of the different functional form in the two theories of the dependence of the quantum yields on the entering ligand concentrations, one of them must fit the experimental data better than the other. In the present case of the $Fe(DTC)_3$ reaction, both theories fit the data equally well within the experimental error of determining the quantum yields.

When [RX] is large and no viscosity dependence is observed, the absence of a viscosity effect can be explained in terms of the nature of the solvent cage. At the large concentrations, the cage itself is primarily composed of RX molecules. Thus neither the forward nor the recombination reaction requires diffusion encounters and the rates will not follow the Debye equation. Because all of the motions are motions within the cage, both the forward and back rate constants will have the same viscosity dependence and the ratio of these constants will be viscosity independent. An alternative explanation is that neither k_1 nor k_2 has any viscosity dependence. However, in view of the dependencies observed at low concentrations, the former explanation is more reasonable.

3. Effects of Coordinating Solvents. Another medium effect which can be quantitatively analyzed using the two theories is coordination of the supporting medium to the reactive metal intermediate. As shown in Figure 1, the intercept of the Noyes plot occurs at a higher RX concentration when a coordinating solvent such as acetonitrile is used instead of a noncoordinating supporting solvent such as benzene. When a better coordinating solvent than acetonitrile is used (such as Me_2SO or pyridine), the halogen abstraction reaction is completely inhibited.

In order to determine if the coordinating solvents could be treated as scavengers of the reactive intermediates in the same manner as were the halogenated hydrocarbons, a Noyes plot of quantum yield vs. the square root of acetonitrile concentration was made (Figure 1c) for constant concentrations of the halogenated hydrocarbon. The linearity of the plots indicates that coordinating solvents compete with RX for the reactive intermediate in eq 1. The resulting complex cannot give the five-coordinated photoproduct. As expected, the kinetic plots are not linear because in the coordinating solvents k_b has components of both RX and acetonitrile and varies with acetonitrile concentration.

Conclusions

The results reported in this paper emphasize the importance of testing all reaction quantum yields for entering ligand and medium dependencies. Only when such dependencies are entirely absent can an observed quantum yield be directly related to some "fundamental" reactivity of the metal complex and compared to theoretical predictions based on excited state bonding changes. When entering ligand or medium dependencies are present, the treatments discussed here may be useful for quantifying the medium dependencies and providing a method of determining the "fundamental" photoactivity and the rate constants.

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