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Photochemistry of Compounds Adsorbed into Cellulose. 3. Kinetic Effects of Matrix in the Quenching of Excited $Ru(bpy)_3^{2+}$ by Chromium(III) Ion[1]

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ABSTRACT: The influence of temperature on both the inherent unimolecular decay of excited $Ru(bpy)_3^{2+}$ and the emission spectrum has been studied from 77 to 295 K. The data obtained in a 50% glycerol/water mixture and glycerol show that $Ru(bpy)_3^{2+}$ can be used as a luminescent probe to observe phase transitions in these matrices. On the other hand, similar data obtained in cellophane show that cellophane provides a medium whose properties change in a monotonous manner with temperature and no phase transition is observed. The quenching of $Ru(bpy)_3^{2+}$ by chromium(III) ion was also studied both in a 50% glycerol/water mixture and in cellophane. The data obtained over the interval from 77 K to the melting point indicate that $Ru(bpy)_3^{2+}$ luminescence is quenched by an energy-transfer mechanism with a second-order rate constant of $(1.2 \pm 0.2) \times 10^6$ mol^{-1} dm^3 s^{-1} at 77 K. At room temperature (295 K), the second-order rate constant and the activation energy are $(1.5 \pm 0.2) \times 10^7$ mol^{-1} dm^3 s^{-1} and 19 ± 2 kJ/mol, respectively. At higher chromium concentrations, above 0.2 mol dm^3, electron transfer is also observed, and the rate constant estimated from transient absorption studies is about 2 orders of magnitude smaller than that for the energy transfer. The decay of excited $Ru(bpy)_3^{2+}$ in the presence of $CrCl_3$ in cellophane obtained at different temperatures in the interval from 77 to 295 K fits well the equation proposed by Inokuti and Hirayama. The parameters obtained are discussed in terms of the distribution of the reacting species of the medium.

Introduction

The past decade has seen an enormous growth of interest in the photochemistry of transition-metal complexes. There are two reasons for this interest: the excited states often give information on the nature of the complexes, and the inorganic complexes provide ideal photosensitizers for many photochemical reactions of direct interest to solar energy.[2] Due to its very suitable spectral properties, having an absorption in the visible part of the spectrum and a relatively long-lived excited state, $Ru(bpy)_3^{2+}$ has received detailed attention. In particular, photoinduced electron transfer from excited $Ru(bpy)_3^{2+}$ to electron acceptors such as methylviologen (MV^{2+}) has been studied by several workers in both homogeneous and microheterogeneous media.[3-8]

$$^{*}Ru(bpy)_3^{2+} + MV^{2+} \xrightarrow{k_1} Ru(bpy)_3^{3+} + MV^{+}\cdot \quad (1)$$

The net result of this reaction is the formation of a $Ru(bpy)_3^{3+}$ complex of reduced methylviologen. In the absence of a sacrificial repair agent such as ethylenediaminetetraacetate (EDTA) which can donate an electron to the $Ru(bpy)_3^{3+}$ giving back the original $Ru(bpy)_3^{2+}$, a fast back-reaction takes place and reduced methylviologen vanishes completely.

$$Ru(bpy)_3^{3+} + MV^{+}\cdot \xrightarrow{k_2} Ru(bpy)_3^{2+} + MV^{2+} \quad (2)$$

However, in cellulose the above reaction was found to take place in a forward fashion to give long-lived reduced methylviologen, even in the absence of a repair agent such as ethylenediaminetetraacetate.[9] This has important implications both for energy storage and for the fundamental theory of electron transfer in reactions such as (1) and (2) above.

Reactions in a cellulose medium are far removed from reactions in simple fluid media as relatively little movement of the species takes place while reaction occurs. Hence, it is of prime importance to reveal some of the properties of the cellulose medium with regard to photoinduced transfer reactions as well as a distribution of the reacting species when absorbed into a cellulose matrix. This paper reports on the properties of photoexcited $Ru(bpy)_3^{2+}$ over a wide range of temperatures in a liquid medium such as 50% glycerol/water as well as a solid state in several different media. The mechanism of quenching between excited $Ru(bpy)_3^{2+}$ and Cr(III) has been studied both in 50% glycerol/water and in cellulose. A comparison between the kinetic data in the two media is then used to discuss the reaction mechanism that takes place for this photoinduced reaction.

Experimental Section

Materials. $Ru(bpy)_3^{2+}$ was obtained from G. Frederick Smith Co., chromium chloride from Fisher Scientific Co., and glycerol from J. T. Baker Chemical Co. All chemicals were used as received. Cellophane film type 215 PD, average thickness 26 μm, was kindly supplied by the Du Pont Chemical Corp., Polymer Products Department. Samples were prepared as described elsewhere.[1] Assuming that all compounds are adsorbed into cellophane as a solid solution, the bulk concentration is expressed in units of mol dm^{-3}.

Instruments. Laser flash photolysis experiments were carried out with a Lambda Physik-100 excimer laser with a wavelength λ = 337.1 nm, a pulse width of 6 ns, and an energy of 8 mJ per pulse and also with a PRA Nitromite laser with the same wavelength as the Lambda Physik laser with a pulse width of 120 ps and an energy of 30 μJ per pulse. Short-lived species were identified by use of rapid spectrophotometric methods involving a Tektronix 7912 AD transient recorder with subsequent computations on a Tektronix 4052A computer. Absorption spectra were measured on a Perkin-Elmer 552 spectrophotometer while luminescence spectra were measured on a Perkin-Elmer MPF-44B fluorescence spectrophotometer. Low-temperature experiments were carried out by cooling the Dewar with N_2 gas which had been previously passed through liquid nitrogen. A desired temperature was achieved by adjusting the N_2 flow. Temperatures were measured with a calibrated copper–constantan thermocouple.

Results and Discussion

Effect of Medium on the Emission Properties and the Luminescence Lifetime of Excited $Ru(bpy)_3^{2+}$. van Houten and Watts have previously studied the effect of temperature and photophysical properties of $Ru(bpy)_3^{2+}$

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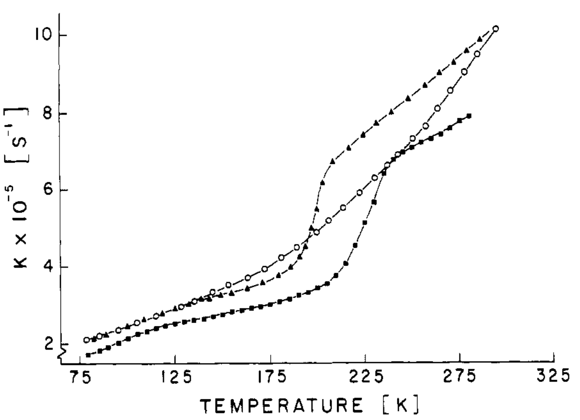

Figure 1. Rate constants for inherent unimolecular decay of excited Ru(bpy)$_3^{2+}$ vs. temperature in glycerol (■), 50% glycerol/water (▲), and adsorbed into cellulose (○). Experimental conditions: λ_{ex} = 337.1 nm, λ_{em} = 610 nm, energy = 30 μJ per pulse.

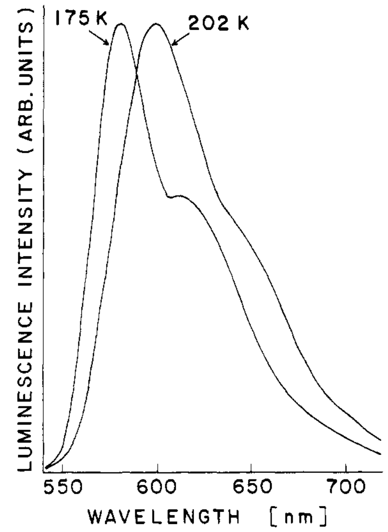

Figure 2. Luminescence spectra of excited Ru(bpy)$_3^{2+}$ in 50% glycerol/water taken at 175 and 202 K. Excitation wavelength = 450 nm.

in aqueous solutions over the temperature range from −196 to 0 °C. They concluded that major changes in the photophysics of this molecule occurred when the medium is transformed from a rigid glass to a fluid.[10] Lytle and Hercules have also reported that the radiative lifetime of Ru(bpy)$_3^{2+}$ in both methanol/ethanol mixtures and 50% H_2SO_4 aqueous solutions decreases significantly around the glass transition points in these systems.[11] This paper expands on this earlier work.

Figure 1 shows the rate constants for the unimolecular decay of excited Ru(bpy)$_3^{2+}$ vs. temperature. Both in glycerol and in 50% glycerol/water mixtures inflection points are obtained which conform to the melting points of these media.

Figure 2 shows the emission spectra of excited Ru(bpy)$_3^{2+}$ in the glycerol/water taken at 175 and 202 K, i.e., just before and just after the melting point in this medium. It can be observed that the peak maximum is shifted ~20 nm and a shoulder at 620 nm which is apparent at 175 K disappears almost completely over the short temperature of 27 K going up to 202 K. From 77 to 175 K the spectrum exhibits a small shift (8 nm) while the shape remains essentially the same.

Figure 3 shows the emission spectra of Ru(bpy)$_3^{2+}$ in glycerol. Contrary to the glycerol/water data over the temperature range 175–202 K, the peak does not change significantly and the shape remains constant. However, the spectrum taken at 231 K after the melting point differs quite markedly from the two spectra described earlier. After the melting point the spectrum neither changes shape nor shows any significant spectral shift on increasing the temperature up to 300 K.

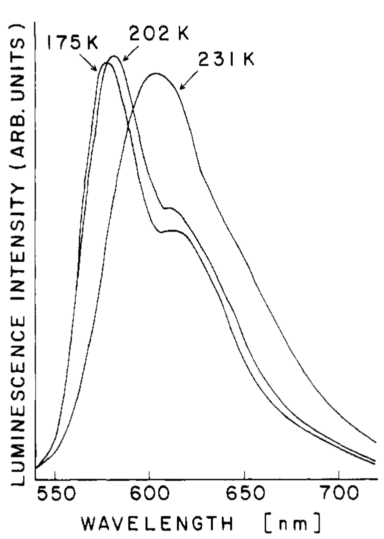

Figure 3. Luminescence spectra of excited Ru(bpy)$_3^{2+}$ in glycerol taken at 175, 202, and 231 K. Excitation wavelength = 450 nm.

Two models are suggested to explain the luminescence from Ru(bpy)$_3^{2+}$, both of which can explain the observed phenomena. Ferguson and co-workers suggest a model which explains the temperature effect on the luminescence spectrum in terms of a distribution of distorted geometries on the complex ion in a rigid glass.[12] The major changes around the melting point are then due to an increased possibility for relaxation in a more fluid state after melting. This could give rise to markedly different luminescence spectra around the melting point.

van Houten and Watts suggested a model which includes charge transfer to ligand states which are modified by mixing with charge transfer to solvent configurations.[10] The solvent deuterium effect indicates that the radiationless decay pathways efficiently dissipate energy through O–H vibrations of the solvent. Hence, the change in the spectral properties around the melting point could be due to a decrease in the energy transfer to solvent in a rigid medium compared to that in a more fluid medium. Either model supports the concept that luminescence properties of Ru(bpy)$_3^{2+}$ show a marked difference around the melting point where the rigidity of the medium changes markedly over a short temperature range and hence, we have intended to use this type of spectral effect to monitor a phase transition in various media.

Figure 1 also shows the data for the rate constant for unimolecular decay for excited Ru(bpy)$_3^{2+}$ when adsorbed into cellophane. The changes with temperature occur in a monotonous manner and no inflection points are observed. The shape of the emission spectrum also changes continuously from 77 K to room temperature and the peak maximum shifts almost linearly with temperature. This leads to the conclusion that cellophane provides a medium whose properties change in a continuous and monotonous fashion with temperature from 77 K to room temperature or close to 300 K.

Quenching of Ru(bpy)$_3^{2+}$ Emission by Cr(III). It has been found earlier that the quenching rate constants of various ruthenium tris(polypyridyl) complexes by Cr(III) did not depend on the redox potential of the system.[13] The ground state of hexaaquochromic ion has the configuration

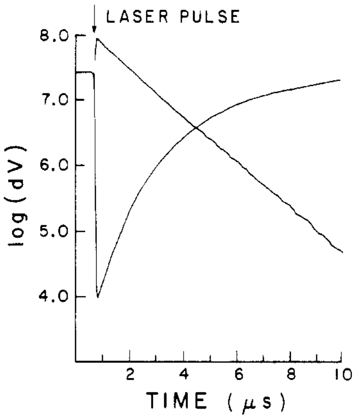

Figure 4. Emission decay of excited $Ru(bpy)_3^{2+}$ at 77 K in 50% water/glycerol glass in the presence of 0.1 mol dm^{-1} Cr(III) (lower line); log (luminescence intensity) vs. time (upper line).

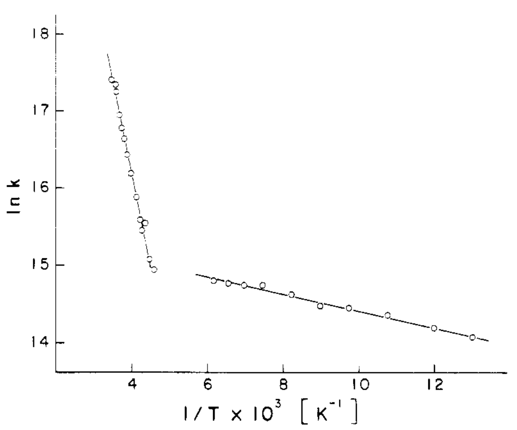

Figure 5. Arrhenius plot for the quenching rate constant obtained in 50% glycerol/water. $Ru(bpy)_3^{2+}$ concentration = 5×10^{-4} mol dm^{-3}, $CrCl_3$ concentration = 0.1 mol dm^{-3}.

${}^4A_{2g}(t_{2g})^3$ and energy transfer to form the excited state ${}^2E_g(t_{2g})^3$, which has an absorption maxima at 630 and 440 nm, is possible. Since all ruthenium complexes have similar emission properties an energy-transfer mechanism is proposed to explain the quenching of excited $Ru(bpy)_3^{2+}$ complexes by chromium. Although an electron-transfer mechanism, as indicated by redox considerations, will not fit the data exactly, it cannot be completely ruled out.[14] In order to elucidate the quenching mechanism further we have extended our studies of the quenching of the excited-state properties of $Ru(bpy)_3^{2+}$ at various temperatures, with the quenching of the excited state over the same temperature range by chromium(III).

A 50% glycerol/water mixture was chosen as a reaction medium because of its convenient properties as indicated earlier, namely, that it forms a clear glass with a distinct transition melting point, and we have previously found it to compare well to cellophane.[1]

Figure 4 shows both the observed decay of excited $Ru(bpy)_3^{2+}$ emission in the presence of 0.1 mol dm^{-3} $CrCl_3$ at 77 K in the glycerol/water mixture and also a semilog plot of the emission vs. time. It can be seen that the data fit a simple exponential plot quite well. An exchange mechanism is proposed for this particular quenching mechanism, which assumes an exponential dependence of the rate constant upon distance. It is tempting to suggest that frozen glycerol/water medium containing $Ru(bpy)_3^{2+}$ tends to exhibit a distribution of ions where similar distances are obtained between all donor and the nearest quencher molecules.

A second-order rate constant, calculated from the equation

$$k = (k_{\text{obsd}} - k_0)/[\text{Cr(III)}] \tag{3}$$

where k_{obsd} is the rate constant in presence of the quencher and k_0 is the rate constant in the absence of the quencher, was found to be 1.2 ± 0.2 mol^{-1} dm^3 s^{-1}. Transient absorption experiments performed in 5×10^{-4} mol dm^{-3} $Ru(bpy)_3^{2+}$ and 0.1 mol dm^{-3} $CrCl_3$ in glycerol/water mixtures at 77 K showed a bleaching of the $Ru(bpy)_3^{2+}$ ground-state absorption which perfectly matches the luminescence emission monitored at 610 nm. There is no resultant removal of the $Ru(bpy)_3^{2+}$ ground state after the excited state has decayed away. This indicates that the quenching of $Ru(bpy)_3^{2+}$ by chromium is probably via energy transfer for this system.

Figure 5 shows an Arrhenius plot for the quenching rate constants. Two slopes can be observed, one which corresponds to the glassy state of the system and gives an activation energy of 1.0 ± 0.2 kJ/mol. Both quencher and quenched molecules are immobilized in the glassy state. Hence, the increase in the rate constant in the interval from 77 K up to the melting point could only be attributed to the change in the Stokes shift which provides a better overlap between the $Ru(bpy)_3^{2+}$ emission spectrum and the Cr(III) absorption spectrum. According to eq 6 this should result in an increase of the quenching rate constant. The second slope, which corresponds to the liquid state, gives an energy of activation equal to 19 ± 2 kJ/mol. The significantly higher value results from a fast diffusion in the liquid state which promotes quenching of molecules in closer proximity. This latter value is similar to the activation energy of self-diffusion in this medium.

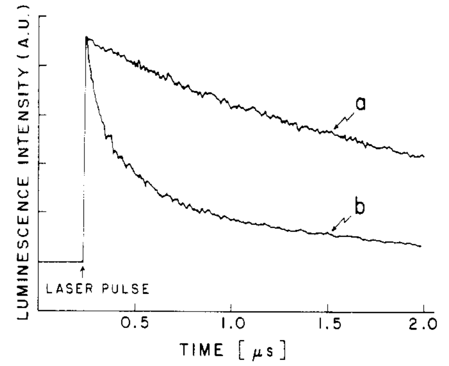

Figure 6. Shape comparison of $^*Ru(bpy)_3^{2+}$ emission decay in the presence of 0.1 mol dm^{-3} $CrCl_3$ at 77 K: (a) in 50% glycerol/water; (b) adsorbed into cellophane.

Transient absorption experiments were repeated at room temperature with the same concentration of $Ru(bpy)_3^{2+}$, $CrCl_3$, and glycerol/water solution as indicated at low temperature, and again ruthenium(III) was not found in the pulsed experiments, indicating that an energy-transfer quenching mechanism is operative at room temperature also.

Quenching of $Ru(bpy)_3^{2+}$ by Chromium Chloride in Cellophane. Figure 6 shows a comparison between the decay of the luminescence of $^*Ru(bpy)_3^{2+}$ in the presence of $CrCl_3$ at 77 K in the glycerol/water mixture and in cellophane.[15] Values in glycerol/water are 5×10^{-4} mol dm^{-3} $Ru(bpy)_3^{2+}$ and 0.1 mol dm^{-3} $CrCl_3$ and in the cellophane are 10^{-2} mol dm^{-3} $Ru(bpy)_3^{2+}$ and 0.1 mol dm^{-3} $CrCl_3$. It is observed that, contrary to the glycerol/water data, the decay of $Ru(bpy)_3^{2+}$ emission in cellophane is of a non-simple exponential form. Due to the thin cellophane film used, 26 μm, high concentrations of $Ru(bpy)_3^{2+}$ (10^{-2} mol dm^{-3}) had to be used. The observed non-simple exponential decay is not due to the higher $Ru(bpy)_3^{2+}$ concentration, as earlier work has shown that quenching by

Table I
$Ru(bpy)_3^{2+}$ Luminescence Quenching Parameters Obtained by Fitting Luminescence Decay Data to Eq 4 at 77 K in Cellophane

$[CrCl_3]$, mol dm^{-3}	$k_0 \times 10^{-5}$, s^{-1}	$\omega \times 10^{-9}$, s^{-1}	$A \times 10^{-3}$
0.05	2.20	1.00	2.51
0.10	2.20	1.01	5.00
0.15	2.20	1.10	7.50
0.20	2.20	1.02	10.2

ground-state and triplet–triplet annihilation does not take place at this concentration at 77 K.[16] The equation derived by Inokuti and Hirayama (eq 4) was used to fit the

$$F_t = F_{t=0} \exp\{-k_0 t - A[(\ln \omega t)^3 + h_1(\ln \omega t)^2 + h_2(\ln \omega t) + h_3]\} \quad (4)$$

emission decay of $^*Ru(bpy)_3^{2+}$ in the presence of Cr(III).[17] This equation was derived by assuming a Dexter type of energy transfer; i.e., the quenching rate constant depends exponentially on distance (r)

$$K(r) = \omega e^{-(2r/L)} \quad (5)$$

L is "effective average Bohr radius" and ω is a factor related to quenching efficiency, expressed by

$$\omega = (2\pi/h)k^2 \int f_D(E) F_A(E)\, dE \quad (6)$$

where k is a constant, $f_D(E)$ is the donor emission spectrum, and $F_A(E)$ is a function connected with the acceptor absorption spectrum.[18] The coefficients h_1, h_2, and h_3 are related to derivatives of the Γ function:

$$\begin{aligned} h_1 &= -3\Gamma'(1) = 1.731\,646\,99 \\ h_2 &= 3\Gamma''(1) = 5.934\,335\,97 \\ h_3 &= -\Gamma'''(1) = 5.444\,874\,46 \end{aligned} \quad (7)$$

A is a linear function of acceptor concentration.

$$A = (\text{const})[Q] \quad (8)$$

Table I shows the parameters obtained by fitting the experimental data obtained at 77 K. It can be observed that the factors k_0 (the rate constant for *Ru(bpy) decay in the absence of quencher) and ω remain constant, whereas A varies linearly with the quencher concentration. The values of the parameters indicate relatively inefficient quenching, which is in agreement with previous observations related to an exchange mechanism.[17] The linear increase of A with quencher concentration indicates a random spatial distribution. The temperature influence on the quenching cellulose was studied by using a sample which contained 10^{-2} mol dm^{-3} $Ru(bpy)_3^{2+}$ and 0.1 mol dm^{-3} $CrCl_3$. The $Ru(bpy)_3^{2+}$ luminescence decays at various temperatures were analyzed by eq 4, and the parameters obtained are presented in Table II. It should be noted that the factor A remains constant.

Table II
$Ru(bpy)_3^{2+}$ Luminescence Quenching Parameters Obtained by Fitting Luminescence Decay Data to Eq 4[a]

temp, °C	$k_0 \times 10^{-5}$, s^{-1}	$\omega \times 10^{-9}$, s^{-1}	$A \times 10^{-3}$	$1/T \times 10^3$, K^{-1}	$\ln(\omega/s^{-1})$
−190	2.25	1.00	5.0	12.05	20.72
−178	2.45	1.30	5.0	10.53	20.98
−165	2.65	1.40	5.0	9.25	21.06
−158	2.80	1.70	5.0	8.70	21.26
−145	3.05	1.81	5.0	7.81	21.32
−132	3.30	2.05	5.0	7.10	21.44
−122	3.50	2.35	5.0	6.62	21.58
−112	3.75	2.45	5.0	6.21	21.62
−99	4.05	2.60	5.0	5.75	21.68
−85	4.45	2.70	5.0	5.32	21.72
−74	5.00	2.80	5.0	5.03	21.75
−52	6.01	3.00	5.0	4.52	21.82
−41	6.50	3.10	5.0	4.31	21.85
−22	7.45	3.20	5.0	3.98	21.89
−15	7.87	3.20	5.0	3.86	21.89
−7	8.40	3.51	5.0	3.78	21.98
+7	9.25	3.60	5.0	3.57	22.00
+15	9.85	3.81	5.0	3.47	22.06

[a] Experimental conditions: cellophane matrix, $[Ru(bpy)_3^{2+}]$ = 0.01 mol dm^{-3}, [Cr(III)] = 0.1 mol dm^{-3}, λ_{ex} = 337.1 nm, and λ_{em} = 610 nm.

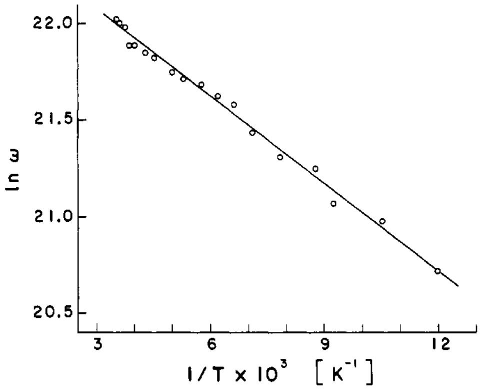

Figure 7. Natural logarithm of the ω factor vs. reciprocal temperature obtained by fitting of experimental $Ru(bpy)_3^{2+}$ emission decay data by eq 4 at various temperatures. Experimental conditions: λ_{ex} = 337.1 nm, λ_{em} = 610 nm, energy = 30 μJ per pulse, $[Ru(bpy)_3^{2+}]$ = 0.01 mol dm^{-3}, $[CrCl_3]$ = 0.1 mol dm^{-3}, cellophane matrix.

Figure 7 shows that the log of ω vs. the reciprocal temperature gives an energy of activation which is 1.2 ± 0.2 kJ/mol, which is similar to the value obtained in glycerol/water glasses. A comparison between the quenching efficiencies in the liquid and solid state of 50% glycerol/water mixture shows that fast diffusion in the liquid state increases the activation energy by a factor of 20. This indicates that no translational motion occurs in the cellophane, although earlier fluorescence polarization data indicate some adjustment was possible.[16] In order to gain insight into the quenching mechanism transient laser flash photolysis experiments were carried out on cellophane containing 10^{-2} mol dm^{-3} $Ru(bpy)_3^{2+}$ and $CrCl_3$ concentrations up to 0.2 mol dm^{-3}. All samples used, apart from the sample which contains 0.2 mol dm^{-3} $CrCl_3$, show a bleaching of the $Ru(bpy)_3^{2+}$ ground state at 450 nm which perfectly coincides with the luminescence emission at 610 nm. However, it is found that the decay of the bleach at 450 nm exhibited two stages in the presence of 0.2 mol dm^{-3} $CrCl_3$, an initial fast component with a similar rate as luminescence at 610 nm followed by a slower decay that corresponds to the back-reaction transfer

$$Ru(bpy)_3^{3+} + Cr^{2+} \rightarrow Ru(bpy)_3^{2+} + Cr^{3+} \quad (9)$$

The same experiment was repeated in water media and again two-stage decay behavior of the bleaching was observed. However, glycerol does not promote such effects. This indicates that the nature of the quenching is controlled by diffusion. If diffusion is fast enough, then the reacting molecules can approach each other to within the distance required for electron transfer before energy transfer has completely taken place. From the absorption data the rate constant for electron transfer in water was estimated to be ~1 × 10^5 mol^{-1} dm^3 s^{-1}. This value is in good agreement with the theoretical prediction made by Sutin and co-workers. They analyzed redox potentials of chromium(III)/chromium(II) and europium(III)/europium(II) couples and their reactivity toward outer-sphere oxidants and estimated a k of electron transfer in such systems of less than or equal to 10^5 mol^{-1} dm^3 s^{-1}.

Conclusions

The present data show two interesting features: (a) that $Ru(bpy)_3^{2+}$ by virture of its luminescence spectrum and excited-state lifetime can be used as a monitor of the rigidity of the medium and (b) that cellophane provides a very convenient matrix whose properties change only monotonously without any discontinuity for the temperature range from 77 K to room temperature. Cellophane provides a medium where no translational motion of the compound absorbed in cellulose is observed. Also, data show that the $Ru(bpy)_3^{2+}$ excited-state quenching by $CrCl_3$ is mainly energy transfer in nature and that electron transfer only takes place when the reacting species are in close proximity. The rate constant for electron transfer is more than 2 orders of magnitude smaller than the rate constant for energy transfer. However, the relative ratio, or the extent of the two reactions, depends quite markedly on the viscosity of the medium.

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Registry No. $Ru(bpy)_3^{2+}$, 15158-62-0; Cr(III), 16065-83-1; cellulose, 9004-34-6; glycerol, 56-81-5; water, 7732-18-5.

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Structural Isomerism in Polycondensates. 2. Aspects for Monomers with Independent Functional Groups

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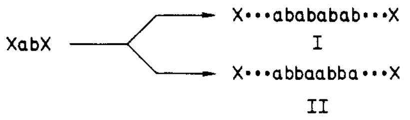
ABSTRACT: Structural isomerism and the possibility to steer structural regularity in homo- and bipolycondensates from at least one homobifunctional nonsymmetric monomer obtained in one kinetically controlled synthetic step are investigated theoretically. The probability of two adjacent nonsymmetric units in a chain to point in the same direction, s, is used to quantify structural regularity. A difference in reactivity between the functional groups of the nonsymmetric monomers is a prerequisite for structural regularity. Furthermore, an important factor determining structural regularity is the relative concentration of these functional groups during the polycondensation. For bipolymers these relative concentrations can be controlled during synthesis, making control of structural regularity possible. For the case of bipolymers from one nonsymmetric monomer, only head-to-head/tail-to-tail regularity can be obtained.

1. Introduction

1.1. Systems Considered.

Linear polymers give rise to structural isomerism if some of their monomeric units can be distinguished in their relative orientation. A sufficient condition for a unit to be distinguishable in different orientations is the absence of twofold rotation axes, except if they are parallel to the "backbone". In the first paper of this series[1] these isomerism phenomena have been quantitatively investigated in some polyamides, both by quantitative chemical degradation and by NMR analysis of the polycondensates. Since the objective of our research is to control the isomerism during polycondensation, we have theoretically investigated the factors influencing structural isomerism during polycondensation. We consider polycondensation reactions of homobifunctional monomers and limit ourselves to the discussion of homo- and bipolycondensates.

In general, structural regularity is determined only to a very small extent by thermodynamic factors. In fact, two polymers consisting of macromolecules of equal chain length and having the regular structures I and II, for instance, can be expected to have somewhat different thermodynamic stability, but the difference is probably small. If polymer I or II is equilibrated with respect to the orientation of the ab units the structural regularity will, in general, be negligible, since the random orientation of



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