Solvent Dependence of the Fast Photooxidation of Transition-Metal Maleonitriledithiolate Complexes, [M(S₂C₂(CN)₂)₂]²⁻ (M = Ni, Pt), in Acetonitrile–Chloroform Mixtures

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The photochemistry of $M(mnt)_2^{2-}$ (M = Ni, Pt) in $CHCl_3$–CH_3CN solvent mixtures was investigated upon excitation in the near-UV region of the spectrum. In both complexes, the quantum yield increased with increasing concentration of $CHCl_3$ up to a limiting value of 0.014 and 0.024 for $Ni(mnt)_2^{2-}$ and $Pt(mnt)_2^{2-}$, respectively, under 365-nm excitation. Similar behavior was observed upon 313-nm photolysis, but in this case, the limiting quantum yields were 0.25 and 0.14 for $Ni(mnt)_2^{2-}$ and $Pt(mnt)_2^{2-}$, respectively. Normalization of the quantum yields with respect to the limiting quantum yield for each wavelength yields identical solvent dependence curves for both complexes indicating that *the solvent dependence is independent of the wavelength dependence*. Picosecond laser flash photolysis was used to probe the fundamental processes occurring in the photooxidation of $M(mnt)_2^{2-}$ (M = Ni, Pt). The picosecond spectra are identical in both halogenated and nonhalogenated solvents. No evidence for primary radicals which could limit yields by geminate recombination is found. It is proposed that the main factor which controls the reaction must be the electronic factor of mixing of the initially excited state with a CTTS state.

Introduction

Over the last few years it has become increasingly clear that there is a large class of photochemical reactions in which the product is determined by events which occur on the time scale of vibrational relaxation or less. Femtosecond time resolution spectroscopy can reveal this directly.[1,2] The major indirect experimental probe is the observation of wavelength dependence across a single electronic band.[3] One common form of such wavelength dependence is a systematic monotonic increase of quantum yield as excitation energy increases with no discontinuities where absorption band boundaries arise. This has been reported to occur in the photochemistry of the title complexes.

Three different types of photoreactivity have been reported for $[M(mnt)_2]^{2-}$ (M = Ni, Pd, Pt; $S_2C_2(CN)_2$ = mnt): (1) Deep UV excitation leads to the initiation of hydrogen evolution from solvents, probably by charge transfer to solvent (CTTS) excitation.[4] (2) A photocurrent at a transparent electrode is observed upon irradiation into the visible region.[5] (3) Near-UV excitation promotes the one-electron photooxidation of $[M(mnt)_2]^{2-}$ (M = Ni, Pd, Pt) in the presence of an electron acceptor[6] (in this case, a chlorocarbon solvent can be reduced.)

$$[M(mnt)_2]^{2-} \xrightarrow[CHCl_3]{h\nu} [M(mnt)_2]^- + CHCl_2^{\bullet} + Cl^- \quad (1)$$
$$\text{photoproducts}$$
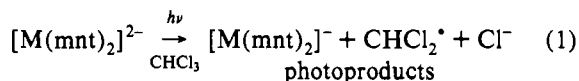
This reaction is the subject of this report. Vogler and Kunkely observed a monotonic increase of quantum yield with excitation energy across absorption bands of different character.[4] There was no evidence of chain reaction initiated by the radicals.

The classical account of such a phenomenon attributes it to competition between geminate recombination and cage escape, but picosecond studies of I_2 dissociation[7] showed some years ago that this view may be oversimplified. As will be seen with the example discussed in this paper, an alternative explanation of wavelength dependence must be considered. The competition between geminate recombination and cage escape is related to solvent viscosity. Vibrational relaxation is important on the short time scale and can be important to wavelength dependent processes. This relates to solvent thermal conductivity. An electron-transfer reaction can have its early stages controlled by solvent dipole reorientation. Thus, solvent effects can provide the clue to the controlling factor.[9–11]

This study has two parts. First, we examine the dependence of quantum yields at two wavelengths as solvent is varied from dilute $CHCl_3$ in CH_3CN to nearly pure $CHCl_3$. Two questions can be answered: (1) Is $CHCl_3$ only a reactant or are the anticipated bulk solvent effects seen? (2) Is the wavelength dependence independent of solvent shell composition? Second, we compare absorption spectra immediately after excitation (picoseconds). This allows us to check some ideas involving the germinate yields in the solvent cage.

Experimental Section

Materials. Spectrophotometric grade acetonitrile and chloroform were purchased from Aldrich and used as received. All other solvents, tetraethylammonium bromide, sodium cyanide, and nickel chloride hexahydrate were reagent grade materials obtained from well-known suppliers and were used as received. The elemental analysis was done by Guelph Laboratories, Guelph, Ontario, Canada.

Sodium maleonitriledithiolate (Na_2mnt) was prepared by a modification of the dicyanodithioformate procedure of Bahr and Schleitzer.[12] A suspension of 10 g (0.61 mol) of finely powdered NaCN in 120 mL

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of DMF was prepared. To this, 30.2 g (24 mL; 0.4 mol) of CS_2 was slowly added with vigorous stirring over a period of 20 min. When the addition was complete, the mixture was stirred for 4 h. The solution was then stored at -10 °C for 24 h. The brown precipitate (sodium dithiocyanate) was collected by suction filtration and air dried. It was recrystallized once from a 1:1 mixture of isobutyl alcohol/isopropyl alcohol. The yield was 18.6 g.

The mnt dianion was obtained by spontaneous dimerization of sodium dithiocyanate in chloroform under an inert atmosphere (7 days). The yellow product was recrystallized twice from 1:1 methanol–ethanol/chloroform. The product was collected by vacuum filtration, washed with 5 mL of cold $CHCl_3$, and air dried. The purity was checked by thin-layer chromatography using a 1:1 acetone–ethanol mixture as the mobile phase. The yield was 19 g (52% based on NaCN). Na_2mnt is a highly electrostatic yellow powder and was stored in a calcium chloride desiccator under nitrogen.

The complexes $[N(C_2H_5)_4]_2[M(mnt)_2]$ (M = Ni, Pt) were prepared according to a published procedure[13] and purified by recrystallization from acetone/isobutyl alcohol three times. The electronic absorption spectra agreed well with those reported previously.[14] Anal. Calcd for $[N(C_2H_5)_4]_2Ni[S_2C_2(CN)_2]$: C, 48.07; H, 6.72; N, 14.02; S, 21.39. Found: C, 48.28; H, 6.52; N, 14.21; S, 20.42.

Steady-State Photochemistry. A 150-W medium-pressure Xenon-arc lamp (PRA Model No. 3402) coupled with an interference filter (Oriel) was used for photolysis at 313 and 365 nm. The 313-nm wavelength is the shortest of those reported in ref 8 for which absorption by $CHCl_3$ is negligible compared to that for the mnt complexes and photochemistry is due to solute absorbance. Solutions of concentrations between 10^{-4} and 10^{-3} M were irradiated in a quartz cuvette (Hellma, 1-cm path length, volume = 3.0 mL) to a conversion of less than 10% in all cases. All solutions were stirred continuously during irradiation. The photoproduct, $[M(mnt)_2]^-$ (M = Ni, Pt), was detected spectrophotometrically at using an HP-8452A diode array spectrophotometer interfaced with an IBM PC. The wavelength of analysis was chosen to be 818 nm since only the photoproduct (i.e. the reduced $[M(mnt)_2]^-$) absorbs in this region. The light intensity entering the photolysis cell at both wavelengths was determined using ferrioxalate[15a] and fulgide[15b] actinometries. The light intensity measured by both actinometers was the same, within experimental error. The standard deviation for all measurements was less than 10%.

Picosecond Spectroscopy. Picosecond time resolved spectroscopy was carried out at the Canadian Centre for Picosecond Laser Spectroscopy at Concordia University. The system is of conventional design and is described in detail elsewhere.[16a,b] Picosecond spectra of $[Ni(mnt)_2]^{2-}$ were recorded using third harmonic Nd/YAG excitation (355 nm) with a pulse energy of 2.3 and 1.7 mJ for $[Ni(mnt)_2]^{2-}$ and $[Pt(mnt)_2]^{2-}$, respectively, and a pulse width of approximately 30 ps. The diameter of the laser beam incident on the sample is approximately 1.5 mm. The probe pulse was derived from a fraction of the exciting pulse. This was focused into D_2O to give a super-broadened probe covering the 425–675-nm range. A delay line enabled the spectra to be recorded at delays from 0 ps to 10 ns after the exciting pulse. The changes in absorbance relative to the spectra obtained without excitation were recorded. The spectra reported are the average of eight recordings. A similar procedure was used for excitation of $[Pt(mnt)_2]^{2-}$; however, the energy was intentionally limited to 1.7 mJ. Solutions of $[M(mnt)_2]^{2-}$ (M = Ni, Pt) used in these experiments were prepared in either 80% (v/v) $CHCl_3$ (20% (v/v) CH_3CN) or neat CH_3CN such that the absorbance at the exciting wavelength was between 0.3 and 0.5 in a quartz cuvette (Hellma, 2-mm path length). Solutions were thoroughly mixed between measurements.

Results

Quantum Yield Measurements. In order to study the relative role of the excitation wavelength, encounter with $CHCl_3$, and the bulk solvent effect on reaction, the quantum yield for photo-
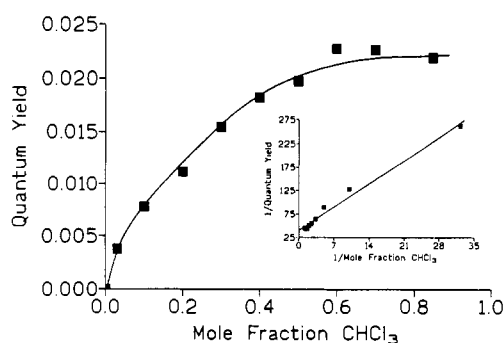
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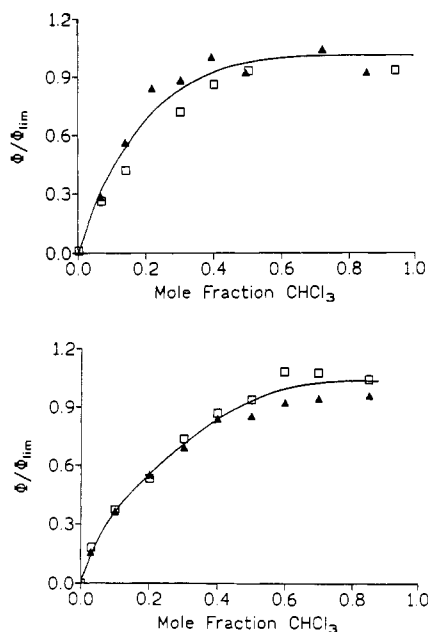
Figure 1. Solvent dependence of the photooxidation of $[Pt(mnt)_2]^{2-}$ using 365-nm excitation in $CHCl_3$–CH_3CN mixtures. The inset shows the double reciprocal plot.

Table 1. Plot Parameters for the Double Reciprocal Plots for $[M(mnt)_2]^{2-}$ (M = Ni, Pt)

wavelength (nm)	$[Ni(mnt)_2]^{2-}$			$[Pt(mnt)_2]^{2-}$		
	R^2	1/slope[a]	Φ_{lim}	R^2	1/slope[a]	Φ_{lim}
313	0.956	1.3	0.25[b]	0.999	0.77	0.14
365	0.991	0.064	0.014	0.988	0.14	0.024

[a] This value equals the initial slope of the solvation curve at low mole fractions of $CHCl_3$ (see eqs 3 and 4). [b] Because the double reciprocal treatment does not produce a good correlation for the case of 313-nm photolysis of $[Ni(mnt)_2]^{2-}$, the limiting quantum yield was estimated as 0.25 directly from the curve in Figure 1.

oxidation of $[M(mnt)_2]^{2-}$ (M = Ni, Pt) using both 313- and 365-nm excitation was examined as a function of mole fraction (χ) of $CHCl_3$ for each irradiation wavelength. A representative curve is shown in Figure 1 (similarly shaped curves were obtained for both complexes under 313- and 365-nm excitation). It is evident that the photooxidation of $[M(mnt)_2]^{2-}$ (M = Ni, Pt) is dependent upon both the solvent and on the wavelength of excitation. The quantum yield for photooxidation of both the Ni and the Pt complexes is essentially zero in CH_3CN and increases with $CHCl_3$ concentration. This establishes the role of $CHCl_3$ as the electron acceptor. A limiting quantum yield is approached at higher $CHCl_3$ concentration. The value of the limiting quantum yield can be estimated by plotting the data in a double reciprocal form ($1/\Phi$ vs $1/\chi$) which linearizes eq 3 below; this aids accurate extrapolation to find the high $CHCl_3$ limit. (The complexes are not soluble in neat $CHCl_3$, preventing experimental measurements at $\chi(CHCl_3) > 0.94$). The equation that describes the system if $CHCl_3$ is simply a reactant which must enter into 1:1 encounter is eq 3. The double reciprocal curve was extrapolated to the reciprocal quantum yield value corresponding to $1/\chi(CHCl_3) = 1$ since this is the maximum mole fraction. In three of these four cases (the 313-nm photolysis of $[Ni(mnt)_2]^{2-}$ was the exception), this procedure gave a statistically very good linear correlation and a fairly precise slope and intercept. A representative plot is shown in the inset to Figure 1. The parameters are summarized in Table 1. In the last case, $Ni(mnt)_2^{2-}$ under 313-nm irradiation, the precise estimation of the parameters required the supplementary assumption that wavelength dependence was independent of solvent dependence as in the Pt case because the plot was noisy. The value of Φ_{lim} for this case was confirmed by direct examination of the high $CHCl_3$ concentration observed yields and calculation of their standard deviation.

We return now to the question of the origin of the expression that describes the chemistry of the system if $CHCl_3$ is acting simply as a reactant and bulk solvent effects are small. Since this reaction involves the transfer of an electron from the metal to $CHCl_3$, an encounter complex must form prior to the event of electron transfer. Thus, the minimum chemistry must proceed according to the following equation, where K_E is the equilibrium constant for the formation of the encounter complex and Φ_{lim} is the intrinsic (and limiting) quantum yield in the encounter
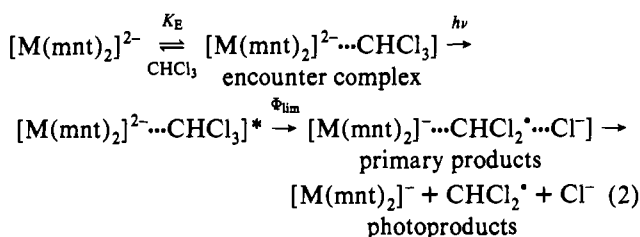
Figure 2. Comparison of the observed solvent dependence for the photooxidation of (a, top) $[Ni(mnt)_2]^{2-}$ and (b, bottom) $[Pt(mnt)_2]^{2-}$ using 313-nm (▲) and 365-nm (□) excitation. Notice the comparability of solvent dependence at both wavelengths. Solvent dependence is not coupled to wavelength dependence.

complex:

$$[M(mnt)_2]^{2-} \overset{K_E}{\underset{CHCl_3}{\rightleftharpoons}} [M(mnt)_2]^{2-}\cdots CHCl_3] \overset{h\nu}{\rightarrow} \text{encounter complex}$$

$$[M(mnt)_2]^{2-}\cdots CHCl_3]^* \overset{\Phi_{lim}}{\rightarrow} [M(mnt)_2]^-\cdots CHCl_2^{\bullet}\cdots Cl^-] \rightarrow \text{primary products}$$

$$[M(mnt)_2]^- + CHCl_2^{\bullet} + Cl^- \quad (2)$$
$$\text{photoproducts}$$

This mechanism leads to eq 3 for the observed quantum yield Φ.

$$\Phi = \frac{K_E \Phi_{lim} \chi}{1 + K_E \chi} \quad (3)$$

Note that Φ_{lim} is a function of wavelength. In eq 3 Φ and Φ_{lim} are the quantum yield and limiting quantum yield, respectively, and χ is the mole fraction of $CHCl_3$.

Evidence for the lack of bulk solvent effects and the separation of solvent dependence from wavelength dependence is obtained by using the yield for the high $CHCl_3$ limit (Table 1), to normalize the quantum yields as a fraction of the limiting value (Φ/Φ_{lim}). This allows direct comparison of the solvent dependence at different wavelengths. Examination of Figure 2 points to identical solvent behavior under both 313- and 365-nm excitation for $[M(mnt)_2]^{2-}$ (M = Ni, Pt). This behavior can be verified by considering the implications of normalizing eq 3:

$$\frac{\Phi}{\Phi_{lim}} = \frac{K_E \chi}{1 + K_E \chi} \quad (4)$$

The slope of the double reciprocal of the normalized curve is equivalent to $1/K_E$.

$$\frac{\Phi_{lim}}{\Phi} = \frac{1 + K_E \chi}{K_E \chi} = 1 + \frac{1}{K_E}\frac{1}{\chi} \quad (5)$$

The normalized double reciprocal plots for $[Pt(mnt)_2]^{2-}$ give good linear correlations (R^2 values for 313- and 365-nm data are 0.997

and 0.984, respectively). The slopes are 0.17 and 0.15 for the 313- and 365-nm data, respectively. The slopes of these curves (and thus K_E) are statistically indistinguishable (using Fisher's Z transformation test[17]). The slope of the normalized double reciprocal plot of the 365-nm photolysis data of $[Ni(mnt)_2]^{2-}$ is 0.22 ($R^2 = 0.991$). However, as mentioned earlier, the 313-nm photolysis data does not yield a good correlation ($R^2 = 0.956$). Thus, the plot parameters cannot be directly evaluated as was done in the Pt case. The value 0.22 is well within our standard deviation of the measured noisy 313-nm slope and suggests that the Ni system is behaving similarly to the Pt system and that K_E is independent of the excitation wavelength. It appears that *the solvent dependence is independent of the excitation wavelength*. That is, there are two separate phenomena. As well, adherence to eq 3, correlation coefficients of 0.99 and slope standard deviations ranging from 1.9 to 9% (in the noisy case), implies that there is little, if any, sensitivity to the significant changes in bulk solvent parameters such as dielectric constant, viscosity, and thermal conductivity that occur between nearly neat CH_3CN and nearly neat $CHCl_3$. $CHCl_3$ is simply a reactant.

Picosecond Spectroscopy. In order to further investigate the role of $CHCl_3$ as a reactant, the spectral behavior at short times was explored using time-resolved picosecond laser spectroscopy. In particular, it is important to know whether the steady-state oxidation yield is substantially lower than the primary yields as a result of recombination. This information is essential to the interpretation of the wavelength dependence because the classical model of wavelength dependence requires initial formation of larger yields of geminate primary products with the overall quantum yield controlled by competition between recombination and cage escape. Unfortunately, the probe pulse and detector do not permit a direct search for the oxidized product at 808 nm. However, bleaching of the band of the starting complex can be examined.

Spectra of both the Ni and Pt complexes in $CHCl_3$–CH_3CN ($\chi(CHCl_3) = 0.723$) mixtures and neat CH_3CN were recorded under identical conditions at various time delays following excitation by a 355-nm, 30-ps pulse. Spectra of the Ni system in a $CHCl_3$–CH_3CN mixture and in neat CH_3CN are shown for delay times up to 100 ps in Figure 3. In both cases, bleaching of the initial ground state band is seen at 475 nm. This corresponds to the depletion of the ground-state absorption upon excitation. A broad excited-state absorption, ESA, band is seen between 525 and 625 nm. This decays within 100 ps to leave a weak residual transient whose intensity remains until 5 ns (in a separate experiment, nanosecond spectroscopy in a $CHCl_3$–CH_3CN mixture where $\chi(CHCl_3) = 0.723$ revealed that there is *no* observable transient (even within the 10-ns pulse) thereby indicating that all of the spectroscopically important excited-state processes occur in the picosecond to short nanosecond time domain). Analogous changes were reported in an earlier study[18] of $[M(mnt)_2]^{2-}$ (M = Ni, Pd, Pt) in the unreactive solvent CH_3CN. These small changes were explained in terms of excited-state processes involving the singlet and triplet metal to ligand charge-transfer status of the complexes. The picosecond spectra are identical in both the reactive $CHCl_3$ and nonreactive CH_3CN solvents (Figure 3). If the primary quantum yield is significantly greater than the observed steady-state yield of 0.014 ($[Ni(mnt)_2]^{2-}$; 365-nm excitation) as required for the classical explanation of wavelength dependency, some evidence should be present in the time-resolved spectrum. Also, it might be expected

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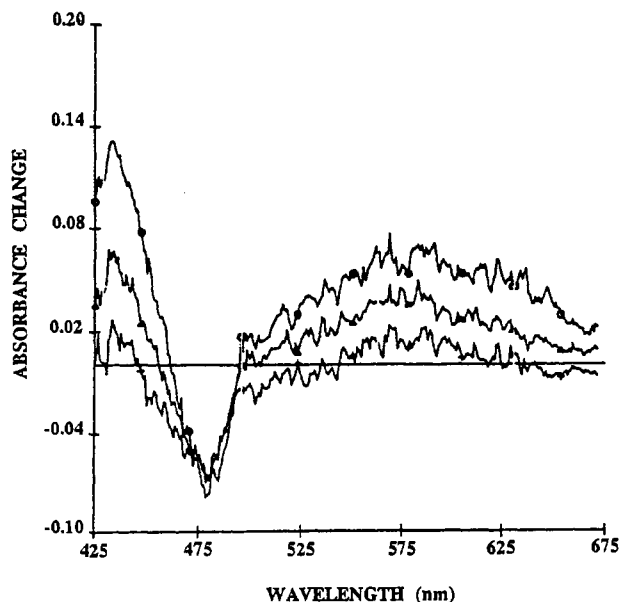
Figure 3. Transient absorption spectra of $[Ni(mnt)_2]^{2-}$ in (a, top) a $CHCl_3$–CH_3CN mixture ($\chi(CHCl_3 = 0.7231$) and (b, bottom) neat CH_3-CN using 355-nm excitation recorded at probe decays of 20, 50, and 100 ps in order of decreasing absorbance change. The pulse energy is 2.3 mJ.

Figure 4. Transient absorption spectra of $[Pt(mnt)_2]^{2-}$ in a $CHCl_3$–CH_3CN mixture ($\chi(CHCl_3 = 0.7231$) using 355-nm excitation recorded at probe decays of (a, top) 50 and 500 ps and (b, bottom) 500 ps and 2 and 5 ns in order of increasing absorbance change of the bleach. The pulse energy is 1.7 mJ.

that the bleach signal in the picosecond spectra would recover on a time scale indicating recombination and not simply reproduce the kinetics of excited-state relaxation in CH_3CN. Thus, it can be concluded that the initial electron-transfer quantum yield must be as low as the overall quantum yield. The small amount of photoproduct ($\Phi = 0.014$) remains nearly undetectable above the noise level of the transient spectra.

Very similar spectra were obtained for the analogous Pt complex in both a $CHCl_3$–CH_3CN mixture and in neat CH_3CN (Figures 4 and 5, respectively) with a broader bleaching feature caused by the breadth of the main visible band of the starting Pt complex. Again, the spectra are very similar to those obtained in the unreactive solvent CH_3CN, which were also explained in terms of excited-state processes.[18] As in the case of the Ni complex, no evidence exists for the primary oxidation of the complex in excess over the overall steady-state irradiation yield (0.024;
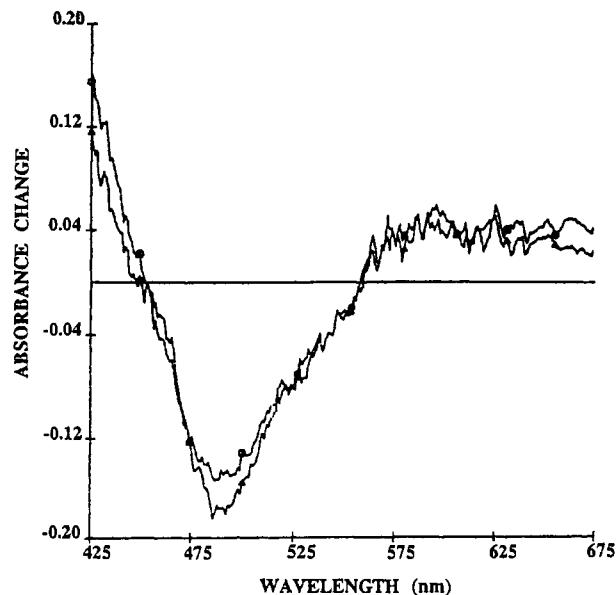
365-nm excitation, as would be required by the classical geminate recombination mechanism). One interesting point regarding the spectra of the Pt complex in $CHCl_3$ is that some recovery of the transient bleach is observed. Furthermore, the transient absorption (betwen 550 and 650 nm) forms within the pulse (30 ps) and does not decay at times as long as 5 ns. This indicates that there is clearly something different occurring in the Pt complex. This concept will be explored subsequently.

Discussion

The balance of evidence from transient spectroscopy suggests that the overall steady-state quantum yields are at most little different from primary transient short time scale yields. Consequently, there seems to be little opportunity to explain the observed wavelength dependence on the basis of the classical competition between radical geminate recombination versus escape from the solvent cage. Moreover, in such a situation, the yield is expected to be reduced by increasing viscosity which means that $CHCl_3$ with a viscosity 1.6 times[19] that of CH_3CN should

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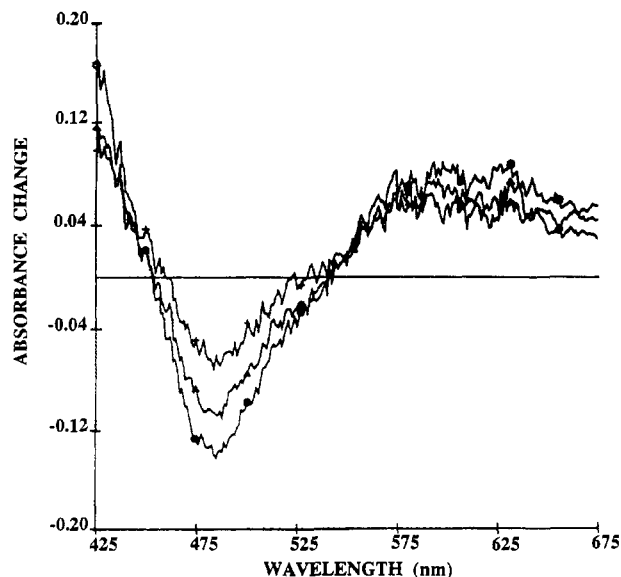
Figure 5. Transient absorption spectra of [Pt(mnt)$_2$]$^{2-}$ in neat CH$_3$CN using 355-nm excitation recorded at probe delays of 500 ps and 2 and 5 ns in order of increasing absorbance change of the bleach. The pulse energy is 1.7 mJ.

retard the reaction. This could lead to a yield downturn rather than leveling at high CHCl$_3$ concentrations or, at least, a more complex mole fraction dependence than the simple linear reciprocal plot. A viscosity change of 1.6× should be detectable with reciprocal plot slopes known to 2–9% uncertainty.

If geminate recombination/cage escape does not explain wavelength dependence, there remain two possible processes in which the solvent is involved that deserve consideration. In the first, the primary product, which consists of a pair of monoanions (eq 2), must be stabilized by solvent reorganization from the solvation shell of the dianionic starting material. A solvent with shorter longitudinal dielectric relaxation time might provide a greater opportunity for this to occur during early (ps) relaxation of the highly excited state achieved on shorter wavelength excitation and thus allow higher yields as a consequence of greater initial excitation. The dielectric relaxation times of CH$_3$CN and CHCl$_3$ are both relatively short[20] (0.19 and 6.4 ps, respectively). But, these relaxation times are ordered in the wrong direction (as with solvent viscosity) to be considered important to the changing yields. Slower dielectric relaxation in CHCl$_3$ would lead to downward deviation from eq 3 as χ_{CHCl_3} increases. Again the nonlinearity should be detectable when $R = 0.99$ and slope standard deviation is 2–9% since relaxation times change by a factor of 30.

The second process in which the solvent plays a major part is dissipation of the excitation energy via vibrational relaxation. In ordinary fluids at room temperature, this is a 10–100-ps process.[10] The major determinant is the "thermal cage" effect which has received extensive attention only recently.[10] A solvent molecule receiving energy from a "hot" center becomes excited and can back-transfer energy in competition with dissipation to the thermal bath. The rate of dissipation will be closely linked to the bulk thermal conductivity. In this regard, CHCl$_3$ is 1.7 times less efficient than CH$_3$CN (the thermal conductivity can be readily estimated, using the equation developed by Sato and Reide,[21] for pure liquids; the values are 4.12 × 10^{-4} and 2.42 × 10^{-4} cal cm^{-1} s^{-1} K^{-1} for CH$_3$CN and CHCl$_3$, respectively).

Vibrational cooling times for dyes have been measured[10] in CHCl$_3$ and CH$_3$OH (which probably models CH$_3$CN adequately) as 35 ± 10 and 13 ± 5 ps, respectively. The implication is that

CHCl$_3$ is approximately two times *less* efficient at dissipating excess energy than CH$_3$CN and the difference between CH$_3$CN and CHCl$_3$ is in the right direction for explanation of the increasing yields. At high initial excitation energy, the reduced rate of loss of excitation in CHCl$_3$ may allow increased probability of crossing to primary product potential surface in competition with relaxation to the ground state, which explains the higher yield under 313-nm excitation. This would carry the interesting implication that the time scale of the reaction is that of vibrational cooling—the 10–100-ps time domain. However, this effect implies an upward deviation from eq 3 and is not supported by the data. In fact, the evidence of the dependence of yield on concentration strongly suggests that neither of the solvent factors is critical to control of the observed yield.

The model leading to eq 3 treats CHCl$_3$ simply as a reactant, the electron acceptor. No effects of changing the *solvent* from CH$_3$CN to CHCl$_3$ are included. The good fit of the data to eq 3 makes clear that all solvent effects are small. Thus, we must conclude that a solvent independent factor is dominant. This factor is electronic. To further our understanding of this reaction, we must seek to comprehend how electronic coupling in the excitation process leads to product formation. Such a discussion can only be speculative so we will keep it restricted to formulating some limiting conditions.

Studies on the photochemistry of iron dithiocarbamato complexes and the carbonyl(η^5-cyclopentadienyl)iron(I) tetramer[22a,b] revealed that near-UV excitation induced an electron-transfer reaction in the presence of a halogenated species. In these studies, it was noticed that the near-UV region of the electronic spectrum was slightly perturbed in the presence of halocarbons (the band intensity increased in the presence of halogenated solvent). Careful inspection of the spectra of these iron complexes in both halogenated and nonhalogenated solvents revealed that this increased absorptivity is due to the presence of an additional transition, probably charge-tranfser-to-solvent (CTTS) in nature. The existence of a CTTS state was verified by an observed dependence of the quantum yield of photoreaction on the wavelength of excitation and the fact that the CTTS maximum correlated with the ease of reduction of the halocarbon. Futhermore, numerous reports[6a,22a,23] (including that of Vogler and Kunkely) have implicated such states in photoreactions of other complexes in chlorinated solvents. Vogler and Kunkely postulated that the photooxidation of [M(mnt)$_2$]$^{2-}$ (M = Ni, Pt) in CHCl$_3$ depends upon a CTTS state but were unable to prove this. Their study focused only on the wavelength dependence of the steady-state quantum yield.

The minimum energy required to reach a CTTS state in which the complex is oxidized and CHCl$_3$ reduced can be estimated from polarographic half-wave potentials, $E_{1/2}$, of the solvent and the complex. (It is important to realize that the one-electron oxidation of [M(mnt)$_2$]$^{2-}$ (M = Ni, Pt) is a reversible process,[6a] whereas the one-electron reduction of CHCl$_3$ is an irreversible process[24].) The polarographic half-wave potential for CHCl$_3$ measures the energy required to reach the unstable primary products, CHCl$_2$$^\bullet$ and Cl$^-$, and is -1.67 V.[25] The oxidation potential of the complex of $E_{1/2}$(Ni) = 0.23 V.[7a] The minimum free energy of the electron-transfer reaction is estimated to be -184 kJ·mol^{-1} from these potentials. The longest wavelength which can supply the minimum energy for this reaction is 650 nm. Vogler and Kunkely showed[6a] that the reaction is not limited to near-UV excitation. Irradiation of [Ni(mnt)$_2$]$^{2-}$ and [Pt(mnt)$_2$]$^{2-}$ with 405-nm light promotes reaction with quantum

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yields of 0.001 and 0.009, respectively.[6a] The low value of the minimum energy suggests that the reactive excited state may be relatively low in energy. The absorption band for a CTTS state would appear as a weak, broad band in the spectrum and would be masked by other intense transitions such as intraligand and LMCT occurring in the same region). The overall quantum yield must reflect either the degree of mixing between the CTTS states and other states or the efficiency of crossing from the initially excited state to the CTTS state. On the basis of the lack of solvent dependence which should arise in any of the relaxation processes, the main factor controlling the reaction is probably the degree of mixing of the CTTS state in the initial transition.