Nuclear Magnetic Resonance Studies of Photochromism. The Photoredox of Tris-*N,N*-dibenzyldithiocarbamatonickel(IV) Bromide

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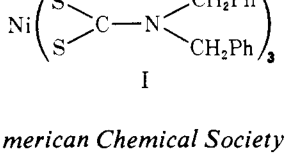
Abstract: An in situ NMR method of directly studying the rate and mechanism of photochromic reactions including both the forward, light induced reactions and the return of the system to equilibrium in the dark is developed. The conditions under which NMR can be used to measure the photostationary state are derived. The method is applied to the photochromic transition metal complex tris-*N,N*-dibenzyldithiocarbamatonickel(IV) bromide. The light reaction involves a one-photon excitation with a quantum yield of ~0.19. No wavelength dependence of the quantum yield is found between 325 and 460 nm. The rate of the light reaction is temperature independent over the range from −4 to +31 °C and is dependent on the solvent and on the concentration of the photoreaction products. All major photoproducts are identified under photostationary state conditions. The back reaction in the dark follows second-order kinetic behavior. The fatigue of the photochromism is defined and discussed.

Photochromism is defined as the light induced reversible change of a single chemical species between two states having distinguishably different absorption spectra.[1] Kinetic studies of the return of the system to equilibrium in the dark (hereafter called the dark reaction) can be accomplished using standard techniques.[2-4] However, studies of the light induced forward reaction (hereafter called the light reaction) are complicated by the concurrent dark reaction and by the possible interference of the promoting light with the method of detection. The latter problem is particularly severe when electronic absorption spectroscopy is used to follow the reactions and the absorption bands of the reactants and products overlap. If the lifetime of the photoproducts is on the order of seconds or less, the system must be monitored continuously, but ir and electronic absorption spectroscopy could be difficult to use because of this interference by the irradiating light. By comparison to all of the spectroscopic techniques, NMR offers the most advantages for studies of photochromism because (1) it does not suffer interference by the irradiating light, (2) it can be used to identify the individual species involved in the reaction, and (3) the changes in the concentrations of the species can be continuously monitored. Its major disadvantage is the lack of sensitivity by comparison with electronic absorption spectroscopy.

Previous studies of the light reactions of photochromic compounds have been reported using electronic absorption spectroscopy,[5,6] and ESR,[7,8] but these studies were limited to systems having light forms stable for several minutes or longer following cessation of irradiation. A side illumination technique[9] was used to successfully study the kinetics of photochromic spiropyrans. NMR identification of transient excited state species of thermochromic spiropyrans has been reported, but no kinetic studies were made.[10] For those spiropyrans exhibiting both photochromism and thermochromism, it was assumed that the excited state species for each were identical.

As part of our program of study of the excited state properties of transition metal complexes,[11,12] we report here direct kinetic data for the light reaction of a photochromic transition metal complex, tris-*N,N*-dibenzyldithiocarbamatonickel(IV) bromide which has structure I. Under the influence of light, the dark brown solution of I bleaches to a very pale yellow-green. On the basis of the kinetics of the dark reaction, the reversible redox decomposition given in eq 1 was suggested to represent the overall reaction.[13]



I

$$\underset{\text{“tris”}}{\mathrm{Ni(R_2DTC)_3}^+} + \mathrm{Br}^- \underset{\text{dark}}{\overset{h\nu}{\rightleftharpoons}} \underset{\text{“bis”}}{\tfrac{1}{2}\mathrm{Ni(R_2DTC)_2}} + \tfrac{1}{2}\mathrm{NiBr_2} + \underset{\text{“thiuram”}}{\mathrm{(R_2DTC)_2}} \qquad (1)$$

The bis complex is diamagnetic while the tris complex is only very slightly paramagnetic ($\mu_{\mathrm{eff}} = 0.7$ for the di-*n*-butyl substituted complex).[13] Therefore the NMR peaks are not extensively contact shifted or broadened and the reaction is amenable to our NMR investigations. Other metal dithiocarbamates have recently been reported to exhibit thermochromism and photochromism.[14] $\mathrm{Ni(Bz_2DTC)_3Br}$ was chosen as representative of the metal dithiocarbamates and used in our studies because of the lack of overlap of the NMR spectra of the light and dark forms of the photochromic complex, the relatively slow dark return rate, and the solubility properties of the reaction products (vide infra). The purpose of this work is to define the conditions under which NMR can be used in in situ studies of photochromism, and to apply the NMR technique to the study of the light reaction (as well as the dark reaction) of photochromic systems.

Experimental Section

Synthesis. Tris-*N,N*-dibenzyldithiocarbamatonickel(IV) bromide, tris-*N,N*-di-*n*-butyldithiocarbamatonickel(IV) bromide,[13,15] bis-*N,N*-dibenzyldithiocarbamatonickel(II),[16] and tetrabenzylthiuram disulfide[17] were prepared by literature methods.

Anal. Calcd for $\mathrm{Ni[S_2CN(CH_2C_6H_5)_2]_3Br}$: C, 51.38; H, 4.03. Found: C, 50.10; H, 4.70. Calcd. for $\mathrm{Ni[S_2CN(CH_2C_6H_5)_2]_2}$: C, 59.70; H, 4.68. Found: C, 60.12; H, 4.78. Calcd for $\mathrm{Ni[S_2CN(C_4H_9)_2]_3Br}$: C, 43.14; H, 7.24. Found: C, 44.12; H, 7.37.

Deuterated acetonitrile was obtained from Bio-Rad Corp. and dried over molecular sieves. No additional purification was carried out on any solvents used for the NMR studies. Distilled solvents were used in obtaining the uv–visible spectra and in the quantum yield determinations.

Instrumentation. The probe of a Varian HR 60 nuclear magnetic resonance spectrometer was modified to allow direct irradiation of the sample in the probe. A 0.4 in. diameter hole was cut in the back of the Faraday shield at the height of the receiver coil. The back panel of the probe containing the coarse and fine adjust paddles was removed. A light pipe arrangement[18,19] was rejected because of insufficient intensity to cause observable spectral changes.

Irradiation was carried out using a Hanovia 1000-W Hg-Xe lamp. A Pyrex lens ($A > 1$ at 325 nm and focal length = 1 m) was used to focus the light beam. For the NMR studies, the full spectral range of wavelengths greater than 325 nm was used to ensure maximum intensity and therefore maximum rates of conversions to the light form. Wavelength dependence and quantum yield studies were accomplished by isolating the 334-, 405-, and 436-nm Hg lines using the filters described in the literature.[20] The 366-nm Hg line was isolated using the Corning glass filter no. CS O-52 and the Gena glass filter no. UG-11.

The quantum yields were determined by following the decrease in the intensity of the 625-nm peak of the absorption spectrum of the tris complex. A small amount of water was added to the acetonitrile to cut off the dark reaction[13] (vide infra). The samples were housed in a thermostated block under the same geometrical restraints as the actinometer solutions. The light intensity was determined by ferric oxalate actinometry.[20] To measure the degree of nonreversibility of the photochromism, the intensity of the 480-nm absorption band was measured. A Hitachi Perkin-Elmer 139 uv-visible spectrophotometer was used for these studies. All absorption spectra were taken on a Cary 14 spectrophotometer.

Because concentrations greater than 10^{-3} M are needed for the NMR signals to be detected, the absorbance of the solutions in the photoactive bands and over all concentrations studied is much greater than unity. Therefore the average number of photons absorbed by the reactant in unit volume and unit time is approximately equal to I_0, the incident intensity, given in photons/s. The incident light intensity on the NMR tube in the spectral range 380-420 nm was 1.8×10^{16} photons/s. In all calculations of the number of photons absorbed, the inner filter effect was considered.[21]

Temperature variations were kept to a minimum by using a quartz Dewar placed inside the NMR probe. During irradiation the temperature increases slowly by a maximum of 3° over a period of 7 min. This temperature variation was the same at all temperatures at which kinetic runs were made. The rate of change of the temperature was approximately 1° during the first minute of irradiation, then 0.5° per minute until the maximum temperature was reached, after which it remained constant. With no cooling the temperature increase was doubled over the same time period and was four times as large over a 15-min irradiation time.

Kinetic Studies. The kinetics of the forward and back reactions were measured by continuously monitoring the disappearance of the α-methylene resonances of $Ni(Bz_2DTC)_3^+$ and $(Bz_2DTC)_2$, respectively. Identical rate constants were obtained when peak heights and peak areas were measured.

Analysis of the Conditions Necessary for NMR Photochemical Studies. The limiting factor in the NMR kinetic method is the concentration of the light form which is a function of the light intensity and the rate constant of the dark reaction (incorporating the temperature dependence of the reaction). For the case of a monophotonic light reaction and an nth order dark reaction given in eq 2,

$$\mathrm{D} \overset{h\nu}{\rightleftharpoons} n\mathrm{L} \tag{2}$$

the concentration of the light form in the photostationary state, L_s is given by eq 3, derived in the appendix,

$$L_s = \left\{\left(\frac{I_0\Phi}{NVk_d}\right)\left[\frac{\left\{1 - \exp(-2.303)\left[\epsilon_D D_0 + \left(\epsilon_L - \frac{1}{n}\epsilon_D\right)L_s\right]l\right\}\left(\epsilon_D D_0 - \frac{1}{n}\epsilon_D L_s\right)}{(\epsilon_D D_0) + \left(\epsilon_L - \frac{1}{n}\epsilon_D\right)L_s}\right]\right\}^{1/n} \tag{3}$$

where D_0 is the initial concentration of the dark form, k_d is the dark rate constant, I_0 is the intensity of the incident irradiation in photons/s, ϵ_D and ϵ_L are the molar absorptivities of the dark and light forms at the wavelength of irradiation, N is Avogadro's number, V is the sample volume, Φ is the quantum yield of the reaction, and l is the path length.

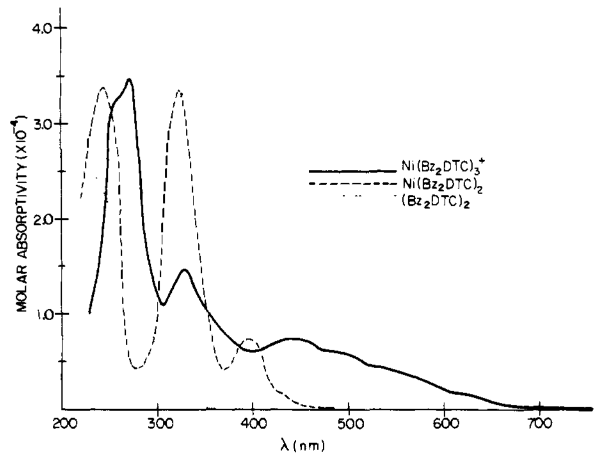


Figure 1. Uv-visible spectra of $Ni(Bz_2DTC)_3Br$, $Ni(Bz_2DTC)_2$, and $(Bz_2DTC)_2$ in acetonitrile. Because of the sensitivity of $Ni(Bz_2DTC)_3Br$ to light and heat, the spectrum must be taken of a fresh solution immediately upon making the solution. The same spectra are observed for all species in $CHCl_3$ as solvent.

No closed solution exists for this expression. By an iterative procedure, however, L_s may be calculated consistent with the known values of the experimental conditions. The spectroscopic parameters necessary to solve eq 3 for the $Ni(Bz_2DTC)_3^+$ system are shown in Figure 1. The spectrum of the bis complex is similar to that of other square planar Ni(II) complexes.[22,23] The average pathlength l for a typical NMR tube is 0.368 cm. For the wavelength region of 380-420 nm, the value of I_0 equals 8.62×10^{15} photons/s. The rate constant of the dark reaction (vide infra) is 0.16 at −4 °C. Substituting these values along with $\epsilon_D = 6.36 \times 10^{-3}$ M^{-1} cm^{-1}, $\epsilon_L = 5.92 \times 10^{-3}$ M^{-1} cm^{-1} and $n = 2$ results in a calculated value of $L_s = 4.58 \times 10^{-3}$ M. Therefore the concentration of the thiuram equals 2.29×10^{-3} M, large enough to be detectable. This concentration requires a 43% decrease in the concentration of the tris complex. Experimentally we observe a 46% decrease.

Results and Discussion

1. NMR Identification of the Photoproducts. The in situ NMR detection of the photochromism allows identification of the photoproducts of the light form without interference from the exciting light. Furthermore, the α-methylene proton resonances of the products were well separated from those of the reactant in contrast with the electronic absorption peaks which are almost completely overlapped. The phenyl proton resonances of the light and dark forms overlapped and showed only minor shift variations between the different compounds and were not used in any of the studies.

The α-methylene resonance of the tris complex ($Ni(Bz_2DTC)_3^+$) occurs at 293 Hz. During irradiation, its intensity decreases and new peaks appear at 281 and 318 Hz. The new peaks were assigned to the α-methylene protons of the bis complex and of thiuram, respectively, by comparison with the NMR signals of pure samples. At −4 °C the intramolecular C-N bond rotation in the thiuram is frozen out and a doublet is observed in the resonances of both the methylene and phenyl peaks.

The signals of the two products do not shift or broaden during the course of the reaction. Furthermore, they remain unchanged in acetonitrile solutions containing equal molar

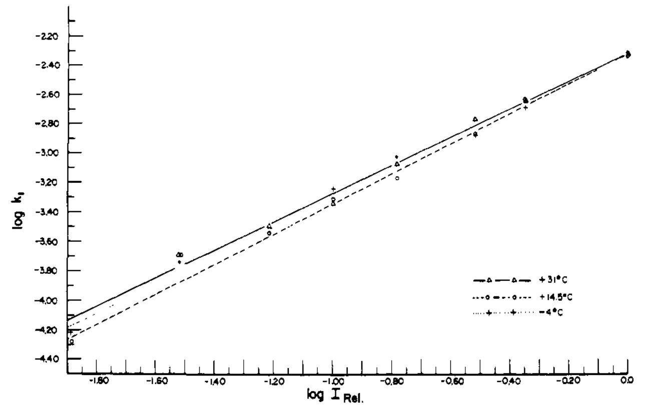


Figure 2. Plots of log k_{obsd} vs. log I_{rel} at 31, 14.5, and −4 °C. At all temperatures, the slopes are nearly unity representing a one-photon excitation step.

Table I. Quantum Yields and Wavelength Dependence of the Light Reaction of the Photochromic Compound $Ni(Bz_2DTC)_3Br$ in Acetonitrile at 23 °C

Bandwidth of exciting light	Φ
330–355 nm	0.162 ± 0.04
350–380 nm	0.18 ± 0.03
380–420 nm	0.22 ± 0.04
420–460 nm	0.21 ± 0.07

mixtures of the two compounds both under irradiation and in the dark at temperatures up to the 60 °C, twice that of the maximum temperatures of the photochemical studies. These results show that there is no intermolecular ligand exchange between the species.

No signals other than those arising from the three compounds discussed above were found in the NMR spectra after careful search of regions of 45 ppm upfield and 10 ppm downfield from Me_4Si. Thus any other species involved in the reactions exist at concentrations below the limit of detection by NMR.

2. **Quantum Yield.** The disappearance quantum yield of the photoredox reaction and the absence of any wavelength dependence are shown in Table I. The values reported in the table were obtained using conventional techniques in a thermostated block. Values obtained by NMR are much less accurate because of the less favorable geometry of the NMR tubes and because of problems of internal reflection. The values determined by NMR agreed within a factor of two with the more accurate ones in the table.

3. **Intensity Dependence of the Reaction.** In a reversible photoreaction in which significant fractions of the incident light can be absorbed by the long-lived photoproducts, it is important to determine whether the photostationary state results from absorption of one photon, or if it is produced via a two-photon process in which absorption of a second photon by a long-lived intermediate is necessary to drive the reaction to completion. The number of photons required may be determined by plotting the logarithm of apparent rate constant of the reaction vs. the logarithm of the relative intensity of the light. A linear plot with a slope of one represents a one-photon process. The results of such a study are shown in Figure 2. Neutral density filters were used to decrease the relative intensity of the incident light and the NMR method was used for detection. The plots are linear with slopes of 0.93 ± 0.04 at 31 °C, 0.98 ± 0.05 at 14.5 °C, and 0.96 ± 0.04 at −4 °C. Thus, the photochromism of $Ni(Bz_2DTC)_3^+$ is a one-photon process.

4. **Temperature Dependence of the Rates.** The dark reactions are second order in the total concentration of Ni(II) in agreement with data previously reported.[13] The rate constants vary from 17.5 M^{-1} sec^{-1} at 45 °C to 0.92 M^{-1} sec^{-1} at 15 °C.

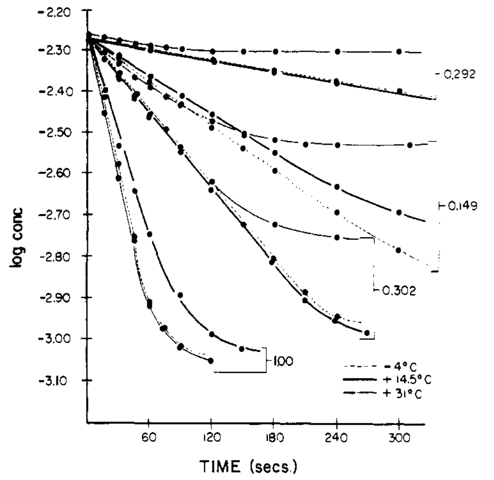


Figure 3. Kinetic plots of log concentration vs. time of irradiation at various temperatures and intensities. The initial rates at a given intensity are equal. The curvature at long irradiation times results from the approach of the system to the photostationary state. At all intensities the runs at 31 °C progress to a lower degree of conversion to the light form than the runs at 14.5 or −4 °C.

The results of studies of the disappearance of the tris complex as a function of irradiation times are shown in Figure 3. As expected, the plot of log $[Ni(Bz_2DTC)_3^+]$ vs. the time of irradiation is linear for short irradiation times. However, linear behavior is not observed during the entire reaction. Departure from linearity results from the approach of the system to the photostationary state (vide infra).

The approach of the system to the stationary state and the relative concentrations at the stationary states are shown in Figure 3 for four representative light intensities and three temperatures. At −4 °C and at light intensities down to 0.149 of the unfiltered light intensity the solutions are driven so far toward the photostationary state that the α-methylene peak of the tris complex can no longer be detected. The limit of detectability of the tris complex by NMR represents >91% conversion to the light form. Under these conditions the total irradiation time needed to complete the photolysis increases from approximately 2 min at full intensity to over 9 min at 0.149 of the total intensity. Linear behavior is observed over the initial 50–80% of the irradiation times. At lower intensities, the initial rate changes after approximately 10% of the total irradiation time. At −4 °C, nearly all of the $Ni(Bz_2DTC)_2$ has precipitated, thus effectively quenching the dark reaction. The reaction is thus able to go to completion over a large range of intensities. At the lowest intensities, the forward reaction proceeds so slowly that the dark reaction effectively competes with the precipitation of the bis complex and a steady state is reached after the NMR signal of the α-methylene peak of the tris complex has decreased less than 40% of its initial height. Even after irradiation of over 1 hr at the relative intensities 0.0292 and 0.0130 the photostationary state remains at the value initially reached.

Because the initial rate constants at −4 °C obtained from the slopes in Figure 3 equal those measured at higher temperatures where there is little or no precipitation, these rate constants accurately represent the kinetic behavior of the light reaction. The rate constants for the light reactions as determined by NMR are given in Table II as a function of temperature and light intensity. The temperature independence of the initial rate is expected if the rate determining

Table II. Relative Rates of the Light Reaction of 5.47×10^{-3} M $Ni(Bz_2DTC)_3Br$ in Deuterated Acetonitrile as a Function of Temperature and Relative Light Intensity[a]

Relative light intensity	$10^3 k_{obsd}$, s^{-1} 31 °C	14.5 °C	−4 °C
1.00	4.7_3	4.5_2	4.7_5
0.450	2.2_4	2.2_9	2.0_1
0.302	1.6_7	1.3_2	1.2_9
0.149	0.82_5	0.67_3	0.92_3
0.100	0.45_6	0.46_2	0.56_4
0.0585	0.31_7	0.28_7	
0.0292	0.20_4	0.20_0	0.18_2
0.0130		0.050_3	0.060_8

[a] The unfiltered output of a 1000-W Hanover Hg–Xe lamp at $\lambda > 325$ nm were used in these studies.

step is the primary decomposition of a molecule of $Ni(Bz_2DTC)_3^+$ in the excited state. This is consistent with the primary step being the loss of one ligand.

At the intermediate temperature of +14.5 °C, the maximum observable conversion of the sample to the light form occurs only at relative intensities greater than 0.302 I_0. Because the dark reaction is faster at this temperature than at −4 °C, it is more competitive with the forward reaction and the photostationary state is reached more quickly and at lower levels of photodecomposition. In contrast, the solution is 90% converted to the light form at +31 °C only at maximum intensity. Decreasing the intensity drastically decreases the extent of the photochromism. For example, at −4 °C, >91% conversion was obtained with light of 0.149 relative intensity, but only 28% conversion is obtained at +31 °C with the same light intensity.

5. Effect of Solvent, Dissolved Oxygen, and Excess Ligand. Addition of tetrabenzylthiuram disulfide to a 5×10^{-3} M solution of $Ni(Bz_2DTC)_3^+$ in a 1:2 mole ratio significantly slowed the rate of the forward reaction and decreased the extent of the light reaction prior to reaching the photostationary state. At a constant relative intensity of 0.149 the reaction rate was lowered from 0.92×10^{-3} to 0.76×10^{-3} s^{-1} at −4 °C even though the photoreaction went to completion. The total irradiation time needed to ensure completion of the photoreaction doubled. Assuming the first step in the photodecomposition involves the loss of one dithiocarbamate ligand which then abstracts a second ligand to form the thiuram, this reaction would be slowed by the initial presence of added thiuram. At +31 °C the addition of the thiuram reduced the reaction rate by 75% from 0.83×10^{-3} s^{-1} to an estimated 0.25×10^{-3} s^{-1}. Only 10% of the sample is photolyzed in the presence of the added thiuram prior to the establishing of the photostationary state as compared to approximately 60% completion without the added thiuram. The decrease is explained by an enhancement of the dark rate by the added thiuram as shown by previous workers.[13] The decrease is not observed at −4 °C because of the precipitation of the bis complex.

In addition to the photoproduced species directly detected by NMR, an undetectable species must be present in order for the system to be reversible. Its necessity is demonstrated by the lack of any dark reaction when only the bis complex and thiuram are both present in solution. One possibility is solvated Ni(II).[13] We have found direct evidence for the participation of Ni(II) by adding a stoichiometric amount of $[Ni(CH_3CN)_6](ClO_4)_2$ to a 1:2 molar ratio solution of the bis complex and thiuram. After addition of the Ni(II), the dark brown color characteristic of the tris complex appears and the resulting solution gives an NMR spectrum identical with that of the tris complex. A careful search for contact shifted acetonitrile was not successful, even in mixed solvent systems such as acetone-acetonitrile where the latter is in at most a 4:1 excess compared to the nickel and any contact shift should be readily apparent. No contact shifted signal was found under the conditions for fast or slow solvent exchange. The minimum concentration of Ni^{2+} required to produce a detectable shift was 0.01 M.

Dissolved oxygen does not participate in the photochromism. The reaction remains reversible and both the light and dark reactions proceed at the same rate in solutions saturated with oxygen and in solutions from which oxygen has been stripped.

No photochromism is observed in noncoordinating solvents such as chloroform.[13] In a 1:1 mixture of CD_3CN-$CDCl_3$ by volume, the light reaction proceeds sufficiently to measure the effect of the solvent change on the reaction rate. The rate constant of the light reaction decreased by 80% from 4.73×10^{-3} to 0.99×10^{-3} s^{-1} at 31 °C and maximum intensity. Furthermore, the degree of conversion to the photostationary state decreased from 90% to 45% upon change of the solvent. The decrease results from decreased solvation of the products $NiBr_2$ and $Ni(Bz_2DTC)_2$.

6. Fatigue of the Photochromism. One of the most important requirements for practical application of a photochromic system is that the reaction be reversible. The lack of complete reversibility, called the "fatigue" of a photochromic system,[24] results in the eventual breakdown of the photochromism. Because fatigue is influenced by physical conditions such as temperature and the intensity of the irradiating light, the fatigue of different photochromic species must be defined under similar experimental conditions. The fatigue of the photochromism of $Ni(Bz_2DTC)_3Br$ is caused by the formation of a residual precipitate. Qualitatively, the amount formed depended on the degree of completion of the reaction. For example, at 31 °C after irradiation for 3-5 min at maximum light intensity (~90% conversion to the light form at the photostationary state), a residual amount of green solid was recovered after the dark reaction. However, when the light intensity was below 0.302 I_0 (less than 50% conversion to the light form at the photostationary state), no residual precipitate was recovered after 10 min of irradiation. The fatigue did not affect the rate constants for either the light or dark reaction.

A quantitative definition of fatigue has recently been proposed.[24,25] It compares the maximum absorbance of the light form at the end of the nth irradiation period in a series of light-dark cycles to that at the end of one irradiation. Because $Ni(Bz_2DTC)_3Br$ is intensely colored in the dark form, we suggest that the change in the absorption spectrum of the dark form rather than the light form be used. For a series of repeated cycles, we can apply the recursion formula given in

$$[D_n] = [D_0]\,(1 - \nu)^{n-1} \tag{4a}$$

$$= 1 - \sum_i y_i \exp(-z_i E) \tag{4b}$$

where $[D_0]$ is the initial concentration of the dark form, $[D_n]$ is its concentration after n cycles, y_i and z_i are unspecified collections of the dark and light rate constants,[25] and E is the total energy of irradiation in the duration of each light cycle. Assuming that Beer's law holds, the logarithmic equation given in eq 5 is obtained.

$$\log \frac{D_n}{D_0} = (n - 1) \log (1 - \nu) \tag{5}$$

Plotting $\log (D_n/D_0)$ vs. n, the fatigue parameter $\log (1 - \nu)$ is obtained. In those cases where curved lines are obtained, the fatigue factor is taken as the slope at $n = 1$. The photochromism of $Ni(Bz_2DTC)_3Br$ exhibits curvature in the fatigue plots. At 27 °C and maximum intensity, the fatigue factor log $(1 - \nu)$ is 2.2×10^{-3} compared to log $(1 - \nu) = 0$ under conditions of no fatigue.

Acknowledgments. We thank the UCLA Research Committee for partial support of this work. One of us (J.I.Z.) gratefully acknowledges the receipt of Camille and Henry Dreyfus Teacher-Scholar Grant (1974–1979).

Appendix

The rate appearance of L is given in eq A1a

$$\frac{d[L]}{dt} = \frac{I_a\Phi}{NV} - k_d[L] \qquad \text{(A1a)}$$

$$I_a = I_0(1 - e^{-\epsilon_D[D]l}) \qquad \text{(A1b)}$$

where I_a is the light absorbed and is defined in eq A1b. Taking into account the inner filter effect and that $d[L]/dt = 0$ at the photostationary state, we obtain eq A2. The symbols are defined in the text.

$$L_s = \left\{\left(\frac{I_0\Phi}{NVk_d}\right) \times \frac{[1 - \exp(-2.303)(\epsilon_D D_s + \epsilon_L L_s)l](\epsilon_D D_s)}{(\epsilon_D D_s + \epsilon_L L_s)}\right\}^{1/n} \qquad \text{(A2)}$$

In general the steady state concentration of the dark form, D_s, is given in eq A3 where n is the stoichiometric number of moles of product per mole of reactant and D_0 is the initial concentration of the dark form.

$$D_s = D_0 - \frac{1}{n}L_s \qquad \text{(A3)}$$

Substituting eq A3 into eq A2 results in the general expression in eq 3 in the Experimental Section. If the absorption spectra of D and L do not overlap and the light reaction can be driven at a wavelength at which L does not absorb, eq 3 reduces to

$$L_s = \left\{\left(\frac{I_0\Phi}{NVk_d}\right) \times \left[1 - \exp(-2.303)(\epsilon_D)\left(D_0 + \frac{1}{n}L_s\right)l\right]\right\}^{1/n}$$

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Reaction of 1-Halonaphthalenes with Nucleophiles by the SRN1 Mechanism of Aromatic Substitution[1]

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Abstract: 1-Halonaphthalenes react in liquid ammonia with several nucleophiles under light or potassium metal stimulation. With acetonate or cyanomethyl anions as nucleophiles, a mixture of the substitution products and products derived from reduction of the naphthalene ring is obtained under potassium metal stimulation. Photostimulated reactions with the same nucleophiles and with alkyl mercaptide ions give the substitution products in high yields. These reactions probably proceed by the SRN1 mechanism. We suggest that the product distribution can be used to determine the structure of the radical anion intermediate formed.

Aryl radicals are intermediates in the recently recognized SRN1 mechanism of aromatic nucleophilic substitution.[2] Supply of an electron to an aromatic compound bearing a suitable leaving group forms a radical anion which then ejects the nucleofugic substituent, emerging as an aryl radical.[3] The radical combines with a nucleophile to form a new radical anion. This radical anion must dispose of the extra electron or otherwise react to form a stable product. It may take another electron, giving reduced products (ketonate anions[4,5] and hydrocarbon derived carbanions[5]), or it may suffer fragmentation (cyanomethyl[6] and ethyl mercaptide anions[7]).

The solvated electron in solutions of alkali metals in liquid ammonia is very effective as an electron source.[8] In other studies, SRN1 reactions stimulated by solvated electrons have afforded fair to good yields of substitution products.[2-6,9] Alternatively, an initiating electron-transfer process can be stimulated photochemically[10] or from electrodes.[11]

Among the aromatic compounds studied, phenyl deriva-