our $(H_3^+)\dagger$ reactant ions may have up to 0.1 or 0.2 eV of translational energy from the trapping fields. It appears to us, however, that the significant difference in results must lie in the uncertainty of the threshold results. Our perusal of Leventhal and Friedman's data indicate at least a 1-eV spread in their reported data points and their assigned threshold is at the extreme upper energy limit of this uncertainty. Thus, the threshold for

$$(D_3^+)\dagger + M \longrightarrow D^+ + M + D_2 \qquad (2)$$

may easily be 1 eV below their stated value of 4.8 eV. If this analysis is valid, then our results agree with Leventhal and Friedman's. If not, the discrepancy remains unexplained.[35]

Acknowledgment. The authors gratefully acknowledge support of the Directors Discretionary Fund of the Jet Propulsion Laboratory, California Institute of Technology.

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(35) NOTE ADDED IN PROOF. Recently, Schiff and coworkers [J. A. Bunt, J. L. Dunn, M. J. McEwan, M. M. Sutton, A. E. Roche, and H. I. Schiff, *ibid.*, **52**, 6062 (1970)] measured the proton affinity of H_2 using a flowing afterglow technique. Their result is $97 \leq PA(CH)_2 \leq 108$ kcal/mol. Since the flowing afterglow technique operates at very high pressures, this result should be appropriate to ground-state H_3^+. By comparison to our results, it appears that $(H_3^+)\dagger$ has of the order of 19 ± 5 kcal/mol internal energy. Huff and Ellisan [N. T. Huff and F. O. Ellisan, *ibid.*, **42**, 364 (1965)] and Christoffersen (R. E. Christoffersen, "A Configuration Interaction Study of the Ground State of the H_3^+ Molecule," Indiana University Theoretical Chemistry Laboratory Report, 1963) calculated the vibrational frequencies of H_3^+ in the equilateral triangle configuration. Both studies are in reasonable agreement and indicate that the symmetric-stretch vibration (A_1') has a frequency of 9.7 ± 0.3 kcal/mol and that the doubly degenerate bend (E') has a frequency of 7.3 ± 0.8 kcal/mol. Hence it appears likely that $(H_3^+)\dagger$ has 2 quanta of vibrational energy and is considerably nonresonant with the vibrational energy of H_2 ($\omega_e(H_2) = 12.5$ kcal/mol). $(H_3^+)\dagger$ is in a metastable configuration and is slowly relaxed to the ground state by collision with H_2 molecules.

Quantum Efficiencies of Transition-Metal Complexes. I. d–d Luminescence[1a]

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Abstract: Quantum yields and lifetimes of six *cis*-$[RhX_2Y_2]^+$ (X = Cl, Br, I; Y = 2,2′-bipyridine or 1,10-phenanthroline) and *trans*-$[RhBr_2(py)_4]Br$ (py = pyridine) are reported. For each complex an intrinsic lifetime, τ_0, a radiative rate constant, k_r, and a quenching rate constant, k_q, were calculated. Evidence for a near-unity intersystem-crossing yield, ϕ_{isc}, for all the complexes is presented, and assignment of the luminescences to a spin-forbidden process is confirmed. A semiempirical spin–orbit-coupling model is shown to predict satisfactorily the intrinsic lives calculated for the complexes from the experimental measurements. Experimental evidence for rapid relaxation between states of different orbital configurations (π–$\pi^* \rightarrow$ d–$\pi^* \rightarrow$ d–d) in transition-metal complexes is presented. Two general rules governing the emission characteristics of transition-metal complexes with unfilled d shells are proposed.

Studies of the luminescence properties of transition-metal complexes with organic ligands comprise a relatively new field of endeavor. Six years ago research was focused on chromium(III) complexes which exhibited a d–d phosphorescence (analogous to that of ruby) and on a few manganese(II) systems. Several preliminary experiments on ruthenium(II) complexes and porphyrin–metal compounds had also been reported. These results were discussed in an interpretive review by Porter and Schläfer.[2] Recently, the literature on transition-metal luminescence has been reviewed by Fleischauer and Fleischauer.[3]

In the last few years large numbers of highly luminescent substances of widely different optical behaviors have been synthesized and studied spectroscopically. Included were a variety of ruthenium(II) compounds which exhibit charge-transfer (CT) luminescence,[4] several osmium(II)[5,6] and iridium(III)[7] compounds which show CT emission, a number of rhodium and iridium complexes demonstrating d–d luminescence,[7,8] and a series of metal–porphyrin complexes showing π–π^* luminescence.[9,10]

The present research was specifically confined to molecular complexes, species whose identities could, in principle, be retained both in the solid state and in a variety of solvents. Our experimental study was undertaken in an attempt to construct a coherent picture of

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the fate of electronic excitation energy in transition-metal complexes and the factors affecting it. Conventional spectrophotometric information (absolute quantum yield, wavelength dependence of the quantum yield, and luminescence decay time) was sought. Central to this work was the determination of the absolute quantum yield, a difficult measurement.[11] Of particular concern were the intersystem-crossing yields and the efficiencies of relaxation among upper excited states. Compounds selected for study were a number of rhodium(III) complexes which display d–d phosphorescence and a variety of ruthenium(II), osmium(II), and iridium(III) complexes which exhibit charge-transfer emission. In the present article we report our results on rhodium(III) compounds and propose some general rules governing the behavior of excited transition-metal complexes. In a subsequent paper (part II of this series), we discuss complexes displaying charge-transfer luminescence. Although all the complexes studied had d^6 electronic configurations, it was our hope that generalizations to other configurations might be made by correlating our findings with the results of other investigations. It is pertinent to summarize briefly and analyze the published literature.

By far the most extensive optical studies on transition-metal compounds have been carried out on chromium(III) complexes. DeArmond and Forster[13] measured the wavelength dependence of the quantum yield of a number of β-diketones of chromium(III).[14] The yields were all very low (less than 2–3%). For most of the complexes the quantum yield was essentially constant regardless of whether excitation was carried out in the lowest energy spin-allowed (d–d) band or the lower energy ligand-localized transitions. Tris(malonato)-, tris(dibenzoylacetonato)-, and tris(benzoylacetonato)-chromium(III) did, however, show significantly lower yields (about one-half) upon excitation in a d–d band *vs.* excitation to the higher energy π–π^* states, an unexpected result. The authors labored to account for the behavior, but the very low yields of these molecules (0.02–0.2%), the great difficulty of obtaining optically pure transition-metal complexes, and the failure of compounds with higher yields to behave similarly prompt us to suggest that the observed behavior was caused by dissociation or by interfering impurities. Major conclusions of their study were, at least in a number of chromium complexes, that relaxation from d–d quartet states and ligand-localized states to the doublet-emitting level proceeds with comparable efficiency and that halogen substitution (chlorine, bromine, or iodine) on the β-diketone ligands has no detectable effect on the intrinsic lifetimes of the chromium d–d phosphorescences from the complexes.

Later Chatterjee and Forster[16] measured the phosphorescence yields and lifetimes of a number of chromium(III) complexes at 77°K. With the exception of $Cr(NCS)_6^{3-}$, which has a yield of 0.23, all the molecules had yields lower than 2% and most were well below 1%. An important conclusion from this work was that relaxation between either of the two lowest spin-allowed states to the spin-forbidden emitting state proceeded with the same efficiency. Also, it was shown that a simple spin–orbit-coupling model could successfully predict the phosphorescence radiative rate constants to within a factor of 10. No direct measurements of intersystem-crossing yields were made, but from the success of the spin–orbit-coupling model and the authors' discussion, we infer that this yield had a value of 0.1 or greater.

Bhatnagar and Forster[17a] surveyed the luminescent properties of a variety of transition-metal ions with oxine ligands. Metals with unfilled d shells (Mn^{2+}, Cr^{3+}, Co^{3+}, Fe^{3+}, Ni^{2+}, and Cu^{2+}) either exhibited no luminescence or ligand fluorescence (in the case of the chromium complex, $^2E \rightarrow {}^4A_2$, d–d phosphorescence). The luminescence yields were all less than 3.5%. Because of these low observed yields and the high fluorescence efficiency of oxine itself, it is our opinion that the fluorescence observed from these complexes having unfilled d shells was very likely luminescence from dissociated ligands in the samples.

Relaxation of excited states in chromium(III) complexes was studied by Camassei and Forster.[17b] Quantum yields and lifetimes of the ^2E luminescence were determined as a function of temperature, and the effect of environment on the nonradiative transitions was assessed. An excitation spectrum of $Cr(CN)_6^{3-}$ doped in a $K_3Co(CN)_6$ host at 93°K was obtained. The results strongly suggest a value of $\phi_{isc} < 1$ for this molecule in this solid matrix, although no corrections of any kind were applied to the raw data to allow a quantitative assessment of the diminution of the yield.

Porphyrins have been studied by Eastwood and Gouterman[9] who carried out low-temperature quantum-yield measurements on complexes of Cu^{2+}, Pt^{2+}, and Pd^{2+}. These molecules exhibit ligand-localized phosphorescence. In contrast to the results of Forster, *et al.*,[17b] the yields were all greater than 0.06, with several approaching unity, and there was no hint of dissociation. The normal strong fluorescence of the free ligands was completely quenched. The evidence points to a high intersystem-crossing yield and a strong heavy-atom perturbation of the emitting triplet (the higher the atomic number of the coordinated metal, the shorter the intrinsic lifetime in a similar series).

Recently Lytle and Hercules[18] measured the absolute yield of tris(2,2′-bipyridine)ruthenium(II) chloride in a rigid glass at 77°K. The yield exceeded 10%, a confirmation of our prediction.[19] In addition the authors reported that the intrinsic lifetime for the emission was independent of temperature in fluid solutions and claimed an intersystem-crossing yield greater than 0.99 for this complex. They also determined a series of quenching activation energies for this molecule in various solvents and attempted to establish the location of spectroscopically nonobserved excited states through a study of quenching phenomena.

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(11) Before undertaking the quantum-yield measurements, a comprehensive literature survey spanning the period 1920–mid 1969 was carried out. The results have been compiled into a critical review article.[12]

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Experimental Section

Preparations, purifications, analyses, proper names, and formulas of the rhodium complexes are given elsewhere.[8] Eosin (Baker Grade) was used without purification as a check on our quantum-yield apparatus and procedure. Rhodamine B (Allied Chemical Co. No. 661) was used (also without purification) in the quantum counter; for yield measurements it was recrystallized three times from a mixture of benzene and methanol. Spectrophotometrically (absorption, emission, and excitation spectra), the two samples of rhodamine B were indistinguishable. Fluorescein, our quantum-yield standard, was Eastman White Label and was purified by the method of Orndorff and Hemmer.[20]

Absolute ethanol and 95% ethanol (both U. S. Industrial Chemical Co., USP-NF) were redistilled, the absolute alcohol from magnesium ethoxide, just prior to use. Absolute methanol (spectrophotometric grade, freshly distilled before use) and ethylene glycol (used without purification) were both Baker Analyzed reagents.

For a low-temperature glass which would hold all the complexes in solution, a mixture of absolute ethanol and absolute methanol (4:1, v/v) was chosen. In the cells employed for our studies this solvent set to a clear, unfractured glass at 77°K.

All absorption spectra were measured on a Cary 14 spectrophotometer. For room-temperature studies on the dyes, matched 10-cm quartz cells were used, and the sample absorbance at the exciting wavelength was kept below 1.0 to avoid fluorescence errors.[21] Low-temperature absorption spectra were run in 1.76-cm i.d. cylindrical Pyrex cuvettes placed in a Pyrex optical dewar filled with liquid nitrogen. In spite of a small cell contraction at 77°K, an effective path length of 1.76 cm was assumed for all temperatures. For computing extinction coefficients at 77°K concentrations were taken as 1.25 times the room-temperature values because of a 20 ± 3% volume contraction upon cooling.

All luminescence measurements were made on an infrared-sensitive spectrofluorimeter constructed in the laboratory and described elsewhere.[8] For the present study several modifications were made. The excitation filters were replaced by an Aminco f/4 grating monochromator blazed at 300 nm. For measuring the relative yield of *trans*-$[RhBr_2(py)_4]Br$ (py = pyridine) as a function of excitation wavelength the cooled infrared-sensitive RCA 7102 photomultiplier was replaced by an EMI 9558QC phototube sensitive in the visible region. For excitation spectra a 1000-W xenon arc was substituted for the 1000-W mercury–xenon arc. The same dewar and unblackened sample cuvettes which were used for low-temperature absorption measurements were also used for all emission studies. In the quantum-yield measurements, liquid nitrogen was kept below the optical paths.

To obtain the wavelength sensitivity of the emission monochromator, the procedure of Parker and Rees[22] was followed; a National Bureau of Standards (NBS) spectral irradiance standard lamp was employed. Because the spectral distribution of the NBS lamp was only given at 50–100-nm intervals, the necessary intermediate data were interpolated from a Wien's law plot. The light from the standard lamp was reflected off a large scatterer (magnesium oxide or Eastman white reflectance paint) into the spectrometer. This arrangement produced an extended source which more closely approximated the emission conditions than the near-point source produced by the standard lamp at a large distance from the spectrometer. A check for any stray infrared radiation which would affect the calibration in the visible range was carried out.

The relative intensity of the excitation source as a function of wavelength was obtained using a rhodamine B quantum counter (8 g/l. in ethylene glycol).[23] This quantum-counter solution was poured into the 1.76-cm cuvette and set in the dewar in place of a sample. The phototube (RCA 2020) viewed the emission from the counter through a Corning 2-59 filter from the back side. This arrangement automatically compensated for all optical paths between the source and the sample.

Relative quantum yields as a function of wavelength were calculated from the formula for $Q_{rel}(\lambda)$, which is shown in eq 1a and 1b, where $Q_{rel}(\lambda)$ is the relative quantum yield at wavelength λ, $I(\lambda)$ is the emission intensity measured at fixed monochromator settings, $E(\lambda)$ is the relative excitation intensity at wavelength λ, $A(\lambda)$ is the absorbance per centimeter of the sample, and L is the path length in the cuvette. In all cases $A(\lambda)$ was held below 0.05/cm to ensure that a relatively uniform emission field was presented to the spectrometer. $A(\lambda)$ was derived from measurements on solutions of higher concentrations which were subsequently diluted quantitatively. The excitation bandwidth was 5.5 nm.

$$Q_{rel}(\lambda) = \frac{I(\lambda)}{E(\lambda)}\frac{1}{1 - 10^{-A(\lambda)L}} \qquad (1a)$$

$$\simeq \frac{I(\lambda)}{E(\lambda)}\frac{1}{2.303A(\lambda)L} \qquad (1b)$$

To obtain relative extinction coefficients as a function of wavelength from excitation spectra we used the relationship

$$\epsilon_{rel}(\lambda) = \frac{I(\lambda)}{E(\lambda)}\left\{\frac{2.303A(\lambda)L}{1 - 10^{-A(\lambda)L}}\right\} \qquad (2)$$

where $\epsilon_{rel}(\lambda)$ is the relative extinction coefficient and the other terms are as defined in eq 1. The term within the braces is a correction for the fact that for values of $A(\lambda)L > 0.01$ the approximations of eq 1b begin to fail. In this work the term within the braces was set equal to unity for $A(\lambda)L \leq 0.01$. To avoid nonlinear behavior, $A(\lambda)$ was kept below 0.05/cm. The excitation bandwidth was maintained at 5.5 nm.

Absolute quantum yields were measured by a modified Parker–Rees method.[22,24] The working equation was

$$Q_x = Q_s\left(\frac{n_x}{n_s}\right)^2\left(\frac{E_s}{E_x}\right)\left(\frac{D_x}{D_s}\right)\left(\frac{1 - 10^{-A_sL}}{1 - 10^{-A_xL}}\right) \qquad (3)$$

where Q is the absolute quantum yield; n, the solvent refractive index; E, the excitation intensity; D, the area under the corrected emission spectrum; A, the absorbance per centimeter at the exciting wavelength; and L, the pathlength of the cuvette. The subscripts x and s refer to the unknown and known, respectively. The technique described by Parker and Rees was employed for estimating D under the actual quantum-yield conditions.[22] In their method D is inferred from the emission intensity measured at a single wavelength and from a corrected emission spectrum run in a separate experiment. The yield and emission experiments were not carried out on the same samples or under identical conditions. To improve the signal-to-noise ratio in the emission experiment, higher concentrations (except for the dyes) and wider excitation bandwidths were used. The same excitation wavelength was used for both measurements, however, and we assumed that the emission spectra of our compounds were not functions of the excitation band pass or the solution concentrations, a reliable assumption for most pure compounds.

The quantum-yield standard was freshly prepared fluorescein (less than 6×10^{-7} *M*) in 0.1 *N* sodium hydroxide at 25°. We assumed the yield to be 0.90, a compromise value from the literature[21,22,25] which is unlikely to be in error by more than 10%. For the measurements on the complexes fluorescein was excited at 436 nm, whereas for comparison with the other dyes excitation of the standard was always at the same wavelength as excitation of the dye (436, 490, or 500 nm).

The refractive indices of the solvents at room temperature were taken from the "Handbook of Chemistry and Physics."[26a] The refractive index of the ethanol–methanol mixture at low temperatures was measured by the method of Deverin and Salzmann.[26b] This procedure utilizes the change in focal length of a microscope which occurs when a medium with a refractive index different from that of air is placed in the optical path. Because of cracking, approximately 110°K was the lowest temperature at which a measurement could be made. Refractive indices on different runs ranged from 1.41 to 1.45. We have assumed the lower value in our computations.

Except for $[RhBr_2(py)_4]Br$, which was excited at 436 nm, all the complexes were excited at 366 nm for absolute quantum-yield measurements. The effective absorbance was taken as the absorbance

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Table I. Quantum Yields, Lifetimes, and Rate Constants for Rhodium Complexes in an Alcohol Glass[a] at 77°K

Complex[b]	Quantum yield, Q, ± std dev	Lifetime, τ, µsec	Intrinsic lifetime,[c] τ_0, µsec	Radiative rate constant, $k_r \times 10^{-4}$, sec^{-1}	Quenching rate constant,[d] $k_q \times 10^{-4}$, sec^{-1}
cis-[$RhCl_2(bipy)_2$]Cl	0.0369 ± 0.0017	31.8 ± 0.5	862	0.116	3.03
cis-[$RhCl_2(phen)_2$]Cl	0.0417 ± 0.0014	33.9 ± 0.6	813	0.173	2.83
cis-[$RhBr_2(bipy)_2$]NO_3	0.177 ± 0.011	18.0 ± 0.3	102	0.980	4.58
cis-[$RhBr_2(phen)_2$]NO_3	0.194 ± 0.018	16.0 ± 0.1	82.5	1.21	5.04
cis-[$RhI_2(bipy)_2$]I	0.55[e]	9.7[f]	17.5[e]	5.71[e]	4.58[e]
cis-[$RhI_2(phen)_2$]I	0.46[e]	10.8[f]	23.7[e]	4.22[e]	5.04[e]
trans-[$RhBr_2(py)_4$]Br	0.0806 ± 0.005	499 ± 2	6200	0.0162	0.184

[a] Unless otherwise specified, all results are for an ethanol–methanol glass (4:1; v/v) at 77°K. [b] Abbreviations of ligands: bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline, py = pyridine. For proper chemical names and formulas see ref 8. [c] Calculated from eq 4. [d] Calculated from eq 5. [e] Estimated values; see text. [f] Data from ref 8; measured in methanol–water glass (4:1; v/v) at 77°K. These substances may decompose somewhat in solution.

at the exciting wavelength (435.8 or 365.5). The relative intensities of the two excitation lines were measured with the quantum counter. The excitation bandwidth for all these measurements on complexes was 3.0 nm.

Blocking filters were incorporated in the instrument to improve the spectral purity of the two excitation lines. At 366 nm a Corning 7-60 and a 0-52 glass filter eliminated stray light, whereas a Corning 3-73 and an Optics Technology 450-nm long-wavelength cutoff filter were employed for the 436-nm line.

Test quantum yields on eosin (in 0.1 *N* sodium hydroxide at room temperature) yielded values of 0.21 (436 nm), 0.22 (490 nm), and 0.23 (500 nm). These numbers are in good agreement with the literature values which group around 0.20.[12] Yields on rhodamine B (in 95% ethanol at room temperature) were 0.71 ± 0.02 (490 nm) for various samples. This value compares favorably with the value measured by Parker and Rees (0.66) which was obtained on a red-sensitive instrument.[22] We are thus led to believe that any systematic error in our measurement procedure is minimal.

Lifetimes were measured on an instrument described elsewhere.[19] The emission filter combination was 1.5 cm of aqueous tris(2,2′-bipyridine)iron(II) chloride (0.6 g/l.) followed by a Corning 2-59 red-pass filter. The excitation filter system was 1.5 cm of $CuSO_4 \cdot 5H_2O$ (100 g/l.) and a Corning 7-60 filter.

Results

Table I shows the absolute yields and measured lifetimes for the complexes at 77°K. The standard deviations for the yields were computed from three or more measurements, all made on different days on freshly prepared samples. The error margins thus indicate the reproducibility and not the accuracy. We believe the accuracy of the yield values to be only within ±30% since systematic polarization errors, quantum-counter variations, and emission-monochromator calibration errors would be reflected in our final values. For the iodo complexes the yields were estimated, and their lifetimes were taken from measurements made in a methanol–ethanol glass (see below).[8]

For each complex an intrinsic lifetime, τ_0, a radiative rate constant, k_r, and a quenching rate constant, k_q, were calculated from the expressions

$$k_r = \frac{1}{\tau_0} = \frac{Q}{\phi_{isc}\tau} \tag{4}$$

$$k_q = \frac{1}{\tau}\left[1 - \frac{Q}{\phi_{isc}}\right] \tag{5}$$

Q is the absolute quantum yield upon excitation to a singlet state, τ is the measured luminescence lifetime, and ϕ_{isc} is the intersystem-crossing yield. In the derivation of these equations the luminescence was considered to be a phosphorescence and quenching was assumed to occur only from the lowest singlet and triplet states in the molecules. Furthermore, to obtain the rate constants and intrinsic lifetimes shown in Table I we assumed $\phi_{isc} = 1$ (for justification, see below).

Although quantum yields were not measured for the iodo complexes, an estimate of the rate constants and intrinsic lives could be made. Inspection of Table I shows that k_q within a series of one type of complex is not greatly affected by changing chlorine to bromine; therefore, it seemed reasonable to assume that k_q for the corresponding iodo complex was comparable to that for the bromo species. With the added stipulation that ϕ_{isc} be set equal to unity, Q, k_r, and τ_0 could be obtained from the measured decay time. (There are some possible complications associated with the iodo complexes. Carstens and Crosby[8] report evidence for decomposition in solution; this possibility introduces additional uncertainty into our calculated values and subsequent correlations for the iodo complexes.)

Figure 1 shows the low-temperature absorption and excitation spectra of the [$RhBr_2(py)_4$]Br complex. Included at the top of the figure is a plot of the relative quantum yield as a function of excitation wavelength. This relative yield is not very accurate below 21 kK (±20%) because the weak sample absorption in this region (0.02 absorbance units) introduces uncertainty in the absorption measurements.

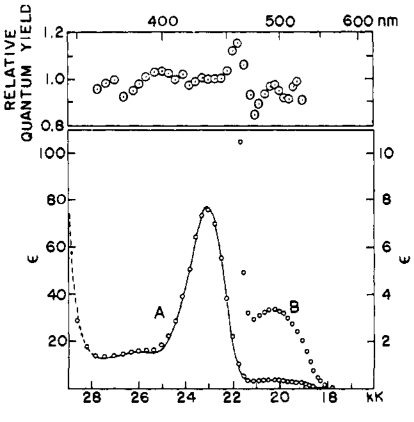

Figure 1. Spectrum and relative quantum yield of *trans*-dibromotetra(pyridine)rhodium(III) bromide: —, low-temperature absorption spectrum; ○, corrected excitation spectra; curve A, left scale; curve B, right scale; ⊙, relative quantum yield. The excitation spectra have been normalized to the absorption spectrum at 23 kK.

Discussion

Confirmation of the Luminescence Assignment. In the computations of rate constants and intrinsic lives, we have assumed that the luminescence is a spin-forbidden process, a phosphorescence. This crucial assumption of a triplet-emitting state in all the complexes deserves further justification. Simple ligand-field considerations predict the lowest excited state in all the molecules to be formally a triplet state which is derived from a $^3T_{1g}$ (d–d) parent octahedral state. A second set of d–d triplets with $^3T_{2g}$ octahedral parentage should lie above this lowest state, followed by a set of singlet states derived from $^1T_{1g}$ and $^1T_{2g}$ (d–d) parent octahedral levels. The ground state is $^1A_1$.[27] In their study of the emission and absorption spectra of a number of rhodium complexes, Carstens and Crosby[8] assigned the luminescences from all the complexes investigated here to a d–d triplet–singlet transition. Their conclusion rested on three lines of experimental evidence: the measured luminescence lifetimes, the existence of an apparent heavy-atom perturbation on these lifetimes, and the large energy separations between the observed emission and absorption bands. We offer here additional quantitative evidence in support of the spin-forbidden assignment.

Table I shows that the *intrinsic* lifetimes of the excited states (with the exception of the iodo complexes) are on the order of 0.1 msec or longer. For the low-atomic-number chloro complexes of cis configuration, the τ_0's are ~1 msec. For the *trans*-[RhBr$_2$(py)$_4$]Br, τ_0 is ~6 msec. These high values strongly suggest a multiplicity change during the emission. Additional support that these measured τ_0 values are indeed reasonable for a phosphorescence and not for an orbitally forbidden (d–d) spin-allowed transition comes from two independent sources, rare-earth and porphyrin studies. Dawson, *et al.*,[28] have measured the intrinsic lifetimes of a series of complexes of terbium and europium, elements having free-ion, spin–orbit-coupling constants comparable to rhodium's. The calculated radiative lifetimes were 0.44 and 2.5 msec, values which are remarkably close to those observed for the rhodium complexes. Since it is well established that rare-earth complexes exhibit a spin- and a Laporte-forbidden luminescence (f–f transition localized on the metal ion), the experimental values suggest a spin change for the rhodium species also. A second support of the assignment arises from the work of Eastwood and Gouterman,[9] who measured the quantum yields and lifetimes of a series of porphyrin–metal complexes. The compounds exhibited a metal-perturbed ligand phosphorescence. Calculating the intrinsic lifetimes by our equations and assumptions but with their data for etioporphyrin complexes of Cu^{2+}, Pd^{2+}, and Pt^{2+}, we obtain radiative lives of 0.12, 3.8, and 0.13 msec, respectively. Again the radiative rate constants calculated for these metal complexes that display a spin-forbidden luminescence are comparable to our values for the rhodium complexes.

Additional quantitative evidence supporting the phosphorescence assignment for the emission observed from rhodium complexes arises from trends in radiative decay constants upon heavy-atom substitution. Changing the halide substituents from chloro to bromo to iodo in the cis rhodium complexes produces a dramatic 40-fold monotonic decrease in the *radiative lifetime*. Such a large effect should not occur if the luminescence were a fluorescence. For example, the study of halogenated fluorescein dyes by Seybold, Gouterman, and Callis[29] showed that replacing up to four hydrogens on fluorescein by bromine atoms had no detectable effect on the intrinsic fluorescence lifetime. Heavy atoms do cause significant changes of phosphorescence lifetimes, however.[30]

Direct evidence for a spin-forbidden assignment for the luminescence of rhodium complexes is shown in the low-temperature absorption spectrum of *trans*-[RhBr$_2$(py)$_4$]Br in Figure 1. A very weak band (ϵ ~3) appears at ~20.3 kK with an intensity $^1/_{30}$th that of the spin-allowed band at 22.9 kK. The position and intensity of this transition lead us to assign it to a $S_0 \rightarrow T_1$, d–d transition. If correctly assigned this measurement would place the energy separation between the absorption and emission maxima of the $S_0 \rightleftarrows T_1$ transition at ~5.7 kK, a Stokes-shift value comparable to that observed for the broad, structureless, allowed d–d transition in chromium(III) (~3.7 kK).[31] The weak band also fills in the large gap between the onset of absorption and luminescence. Further evidence that the emissions observed from rhodium complexes are spin forbidden comes from a simple semiempirical spin–orbit-coupling model for rationalizing the radiative lifetimes derived from our measurements (see below).

Because of the accumulated evidence the phosphorescence assignment for the rhodium luminescence appears to be firm. This identification is assumed in all subsequent discussion and data correlations. We also assume that the 20.3-kK band in [RhBr$_2$(py)$_4$]Br is the inverse of the luminescence, *i.e.*, the lowest singlet–triplet absorption band in the molecule.[32]

Intersystem-Crossing Yields. Of key theoretical and experimental importance are the values of the intersystem-crossing yields (ϕ_{isc}) in complexes. Figure 1 shows the relative quantum yield of [RhBr$_2$(py)$_4$]Br as a function of excitation wavelength. The yield is essentially constant when excitation is accomplished either in the spin-allowed bands or in the spin-forbidden band, a result which shows that the intersystem-crossing efficiency is near unity. Since the relative yield measured at 20 kK is accurate to ±20%, we conclude that ϕ_{isc} in this rhodium complex is within 30% of unity and infer that it is unity. This is the first direct measurement of ϕ_{isc} in a molecular complex exhibiting d–d phosphorescence. Because of the obvious similarities between the spectroscopic properties of this molecule and the rest of the complexes, we have assumed that a high intersystem-crossing yield prevailed in all the other rhodium complexes studied.

As we shall show in part II of this series near-unity intersystem-crossing yields at 77°K appear not to be

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(32) Because of the magnitude of the spin–orbit interactions, this triplet upper state is certainly split by a substantial, but as yet undetermined, amount.

unique to second-transition-series complexes exhibiting d–d luminescence; second- and third-transition-metal complexes exhibiting charge-transfer phosphorescence also appear to have $\phi_{isc} \simeq 1$, although ϕ_{isc} does not have a clear meaning for the heavier molecules, and reasonable alternate interpretations of the measured ϕ's exist (see part II). There is, in addition, some persuasive indirect evidence that ϕ_{isc} is very high, even in metal complexes of the first-transition series. These lines of evidence stem from two sources, photochemistry and the unusual emission properties of chromium(III) complexes.

The room-temperature photochemical studies of a variety of chromium(III) complexes provide evidence for the complete conversion between upper excited quartet states and the lowest excited doublet state of the ion. Several complexes which have only one photochemical reaction mode and a constant quantum yield when excited in any of the quartet–quartet absorption bands also have the same reaction mode and the same quantum yield when excited directly to the doublet state; the yields are significantly less than unity.[33] The most reasonable explanation of these data is that all excited molecules relax with near-unity internal-conversion and intersystem-crossing yields to the lowest doublet state, from which they deactivate by chemical decomposition or radiationless decay. Thus, experimental data suggest that $\phi_{isc} \simeq 1$ for at least several chromium(III) complexes at room temperature. We point out that not all chromium complexes exhibit such simple behavior. A number show more than one reaction mode, and the photochemical yields are strongly wavelength dependent.[33] Clearly, such behavior cannot be described by the simple kinetic scheme implied above.

The hexacyanocobaltate(III) anion also appears to have an intersystem-crossing yield on the order of unity. This complex photoaquates with a wavelength-independent yield of 0.3 when excited in either of the spin-allowed d–d absorption bands.[33] Porter[34] has shown this yield to be ~0.23 when the complex is excited indirectly by intermolecular energy transfer from optically excited biacetyl. Since the triplet state of biacetyl (~20 kK) is certainly below the complex singlet level, direct population of the triplet level of the complex by energy transfer was inferred. The quantum yield for photoaquation is thus comparable for excitation to the singlet states or to the triplet state. The most reasonable explanation for these results is that the reactive species is the complex in its lowest state and that the intersystem-crossing yield approaches unity.

The low-temperature luminescence from a variety of chromium complexes supplies further credence to a picture of rapid interconversion of states of different multiplicities in complexes. It has been found that chromium(III) complexes can exhibit fluorescence, phosphorescence, or both simultaneously depending on the crystal-field strength of the surrounding ligands. An explanation based on the pseudothermal equilibration of the lowest quartet and doublet states, originally proposed by Schläfer, Gausmann, and Witzke[31] was subsequently expanded by Hempel and Matsen,[35] whose conclusions can be summarized as follows. The observed fluorescence-to-phosphorescence ratios in luminescent chromium(III) complexes can be explained quantitatively by assuming that a pseudo-Boltzmann equilibrium exists between the ^2E and $^4T_2$ potential minima. The establishment of pseudoequilibrium, however, is only possible if the intersystem-crossing rate constant is much higher than any of the other rate constants for depletion of these two states. This, in turn, implies that the ϕ_{isc} must approach unity.

Metals with d^{10} electronic configurations frequently form highly fluorescent complexes (for example, zinc porphyrin compounds[10] and oxine complexes of zinc and cadmium[17a]). These are examples of transition-metal complexes possessing a ϕ_{isc} which is obviously not unity. There is also some evidence for $\phi_{isc} < 1$ in complexes containing metals with unfilled d shells, because ligand fluorescence from them has been reported.[17a] Since a slight dissociation of the complexes could have produced the observed results, however, the evidence is not impeccable.

The available direct measurements of ϕ_{isc} (with the possible exception of the hexacyanochromate species), the photochemical evidence for unity ϕ_{isc}, the apparent pseudo-Boltzmann equilibrium established between the excited states of chromium(III) complexes, and the lack of firm contradictory evidence lead us to postulate the following rule. *In the absence of photochemistry from upper excited states, emission from a transition-metal complex with an unfilled d shell will occur from the lowest electronic excited state in the molecule or from those states which can achieve a significant Boltzmann population relative to the lowest excited state.* Although this rule has been inferred from data on a relatively small sampling of d^3 and d^6 complexes and must be regarded as tentative, it is our opinion that the assertion will be valid for most transition-metal complexes with unfilled shells.

We wish to emphasize that emission may not be observed from many complexes. In species possessing energy-level patterns with no large gaps between levels, radiationless processes may deplete all states before emission can occur.[5]

Relaxation Efficiencies. Since excited states of several different orbital promotional types, *i.e.*, π–π^*, d–π^* (or π–d), and d–d, exist in metal complexes, it is of interest to ascertain the relative efficiencies of relaxation between excited states of various orbital designations. Unfortunately, owing to instrumental limitations we were unable to make a direct measurement of the relaxation efficiency between a π–π^* state and a lower d–d state in a complex; we can, however, infer probable efficiencies. As shown in part II, efficient (unity) internal conversion between π–π^* ligand-localized and d–π^* charge-transfer states occurs. This efficient relaxation might be attributable to the common d component in the wave functions for both states. The observation of a unique d–d luminescence obtained by pumping adjacent CT states indicates that relaxation from charge-transfer states to d–d states also proceeds with high efficiency.[36] A similar cascade mechanism seems likely. It is not obvious, however, that relaxation between π–π^* and d–d states would necessarily be an efficient process, because in many molecules neither

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type of state wave function contains a high degree of admixture of the other kind. The observed transitions closely reflect their parentage. Relaxation might be hindered and upper-excited-state emission or quenching directly to the ground state might occur. Even if direct relaxation from $\pi-\pi^*$ to d–d states were hindered, however, the presence of a charge-transfer state between the $\pi-\pi^*$ and the d–d states could provide an efficient relaxation mechanism ($\pi-\pi^* \rightarrow$ d–$\pi^* \rightarrow$ d–d). Fast relaxation from $\pi-\pi^*$ to d–d states will probably be the most common situation, since molecules with low-lying $\pi-\pi^*$ states also tend to have lower lying d–π^* states.

DeArmond and Forster[13] have presented some evidence for efficient direct energy degradation from $\pi-\pi^*$ to d–d states in a chromium(III) complex, although they could not supply unequivocal electronic descriptions of the upper excited states. They suggest, however, that the upper levels were ligand-localized $\pi-\pi^*$ states. A firm answer to this question of the efficiency of $\pi-\pi^*$ to d–d relaxation cannot yet be stated. The results and arguments are not strong, but they do indicate that $\pi-\pi^*$ to d–d relaxation is an efficient process. We propose the following rule. *If no photochemistry occurs from upper excited states, transition-metal complexes with unfilled d shells will exhibit wavelength-independent quantum yields.* This rule must be regarded as tentative; further experimental evidence is certainly needed.

Rate Constants. It is possible, and of considerable interest, to evaluate the rate constant for intersystem crossing (ϕ_{isc}) in metal complexes. Since our complexes are nonfluorescent it is not possible to determine k_{isc} directly, but one can make reasonable estimates of lower limits.

To our knowledge, there has been no direct measurement of the radiative rate constant for a d–d fluorescence. We need, therefore, to estimate k_f, the rate constant for fluorescence deactivation of the singlet state. For most organic molecules ($\pi-\pi^*$ fluorescence) k_f is typically greater than 10^7 sec^{-1}, but this value cannot be transferred to d–d fluorescences, since the latter are orbitally forbidden (in a crystal-field model involving pure d wave functions). If it is assumed, however, that k_f/k_p (where k_p is the rate constant for radiative depopulation of the lowest triplet state) is equal to the ratio of the maximum extinction coefficients of the spin-allowed and the spin-forbidden bands, an upper limit to k_{isc} can be obtained. For $[RhBr_2(py)_4]Br$, k_f/k_p is about 20; k_f then equals 3×10^3 sec^{-1} (see Table I). In spite of the broadness of the phosphorescence band, it is reasonable to assume that the fluorescence-to-phosphorescence ratio could not have exceeded 1/100 and escaped our measurements. Since the phosphorescence quantum yield, ϕ_p, is $\sim$0.1, the fluorescence yield, which is related to the rate constants by eq 6, must be less than $\sim 10^{-3}$.

$$\phi_f = \frac{k_f}{k_f + k_{isc}} \tag{6}$$

We have explicitly assumed here that direct quenching from the singlet state to the ground state is negligible, an assumption which is supported by our previous observation that ϕ_{isc} is $\sim$1.0. Substitution of the estimated values of ϕ_f and k_f into eq 6 yields $k_{isc} \geq 3 \times 10^6$ sec^{-1}.

For *cis*-$[RhBr_2(bipy)_2]^+$ (bipy = 2,2′-bipyridine) a similar analysis is possible if we again assume $k_f/k_p = 20$. Although there is no direct experimental justification for using this value, the similarity of the two bromo complexes leads us to believe that 20 is a reasonable lower bound. An analogous calculation (assuming that $\phi_f/\phi_p \leq 1/100$ and $\phi_{isc} = 1.0$) gives $k_{isc} \geq 10^8$ sec^{-1}.

For complexes that contain ruthenium atoms and exhibit charge-transfer luminescence, k_{isc} may possibly be greater than 10^{10} sec^{-1} at 77°K (see part II). Because of the comparable spin–orbit-coupling values for ruthenium and rhodium (ξ_d for rhodium is actually significantly greater than ξ_d for ruthenium), we believe that k_{isc} for our rhodium complexes is probably comparable to that for ruthenium ($\geq 10^{10}$ sec^{-1}), although direct experimental evidence for the value is lacking. It is probable that all second- and third-transition-series complexes which possess unfilled d shells have comparable values of k_{isc}.[37]

The $S_0 \rightarrow T_1$ transition in *trans*-$[RhBr_2(py)_4]Br$ is well resolved in absorption at 77°K (Figure 1). It was thus possible to show whether the Strickler–Berg formula[38] for obtaining intrinsic lifetimes from absorption data could give reasonable estimates of this quantity. The corrected excitation spectrum of Figure 1, also taken at 77°K, was assumed to approximate the low-temperature absorption spectrum. The calculated τ_0 from the Strickler–Berg formula is 130 μsec,[39] which compares very poorly with the measured value of 6.2 msec. The correct application of this formula for our case is not clear, however. The degeneracy ratio, g_u/g_l, could lie anywhere between one and nine, depending upon the nature of the absorption band, the orbital and spin descriptions of the excited state, and the magnitudes of the actual splittings in comparison with kT. We arbitrarily chose g_u/g_l equal to unity.

Phosphorescence Lifetimes. A Spin–Orbit-Coupling Model. The heavy-atom effect on the phosphorescence decay times of halogen-substituted aromatics has been explained semiquantitatively by McClure using a simple spin–orbit-coupling model.[40] Reasonable agreement between the predicted trends and the experimental results was achieved even though radiative lives (τ_0) handled by the model were compared with measured lives which included an unknown component due to quenching.[30,40]

For testing the appropriateness of a spin–orbit-coupling model for correlating radiative decay constants of complexes, we adopted a modification of McClure's procedure which correlates the radiative decay time (τ_0) of the phosphorescing (triplet) state in a series of similar compounds to the largest atomic spin–orbit-coupling constant (ξ) for the electron most involved in the transition by the equation

$$\frac{1}{\tau_0} = K\xi^2 \tag{7}$$

K is a proportionality constant which is specific to the series.

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[37] The quantity ϕ_{isc} loses some meaning for very heavy atoms since spin–orbit coupling becomes important and S becomes a poor quantum number. In such cases, the terms intersystem crossing and internal conversion as defined in ref 15 become indistinguishable.

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[39] The parameters used in the calculation were $\bar{\nu}_{max}$ 20.3 kK, ϵ_{max} 3.3, $\bar{\nu}_{1/2}$ 2.8 kK, and $\langle\lambda^3\rangle^{1/3}$ 704.8 nm; $g_u/g_l = 1$.

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The cis-substituted dihalo complexes of rhodium(III) with 2,2′-bipyridine and 1,10-phenanthroline provide a good test for the spin–orbit-coupling model (Table I). The use of only the largest atomic spin–orbit-coupling constant in the computation is not justified, however, because in a chloro complex the metal has the largest ξ, whereas the ξ value for bromine is comparable to that of rhodium. In an iodo complex iodine has the largest spin–orbit-coupling constant. It appears reasonable to assume as a first approximation that the lifetime is influenced by the average of the square of the spin–orbit-coupling coefficients over the atomic centers influencing the electron involved in the transition. We thus obtain

$$\frac{1}{\tau_0} = \frac{K}{7}\sum_{j=1}^{7}\xi_j^2 \qquad (8)$$

The seven centers include the metal and the six nearest ligand atoms. Ignoring the other atoms in the complexes appears reasonable because the luminescence is d–d in character and the optical electrons would be expected to feel the presence mainly of the surrounding six nearest neighbors and the metal ion. Possible refinements of the model are obvious, but the paucity of data to date does not warrant destroying its appealing simplicity.

The inclusion of ξ's only for the central metal and its nearest neighbors is also justified by the results. Because of the structural similarities of the complexes this model predicts that the intrinsic lifetimes of analogous 2,2′-bipyridine and 1,10-phenanthroline species should be the same. Table I shows the remarkable result that this prediction is verified. In fact, it was possible to determine a mean value of K appropriate for both series of complexes semiempirically from the average of the experimental τ_0's of the *cis*-bromo complexes and appropriate spin–orbit-coupling constants.[40,41] (The ξ for a p electron on chlorine was assumed to be 0.587 kK, for bromine 2.46 kK, and for iodine 5.06 kK. For trivalent rhodium an extrapolated value of 1.55 kK (ref 41, p 60) was used.) Substitution of these quantities in eq 8 yielded a value for K of 5.22×10^{-3} μsec^{-1} (kK)^2, which was then used to predict τ_0 values for the cis complexes containing chlorine and iodine. The values of τ_0 from the model are compared with those derived from experiment in Table II. Semiquantitatively the agreement is excellent; the experimental τ_0's change by a factor of 40, yet the calculated τ_0's all agree with the measured ones to within a factor of 2.

Table II. Calculated and Observed Intrinsic Lifetimes of *cis*-Dihalo–Rhodium Complexes

Compound (77°K)	τ_0(calcd),[a] μsec	τ_0(exptl), μsec
$[RhCl_2(bipy)_2]Cl$	434	862
$[RhCl_2(phen)_2]Cl$	434	813
$[RhBr_2(bipy)_2]NO_3$	92.3[b]	102
$[RhBr_2(phen)_2]NO_3$	92.3[b]	82.5
$[RhI_2(bipy)_2]I$	25.0	17.5
$[RhI_2(phen)_2]I$	25.0	23.7

[a] Calculated from eq 8. [b] Average of the experimental τ_0's for the two bromo complexes. This value was used for generating K in eq 8.

An attempt to predict the radiative life of the *trans*-$[RhBr_2(py)_4]Br$ complex by means of the K appropriate for the cis series failed. The predicted τ_0 is ~0.1 msec; the experimental τ_0 is ~6 msec. The failure is not surprising, since the molecular symmetries are very different (the emission is only spin forbidden in the cis complex, but it is orbitally and spin forbidden in the trans species). Nevertheless, it seems reasonable to expect that a new K determined for the *trans*-dibromo complex would apply to the entire series of *trans*-dihalo pyridine complexes. The K calculated from this trans species is 7.78×10^{-5} μsec^{-1} (kK)^2. Unfortunately, because of experimental problems we can only cite qualitative experimental data to test the validity of the model for a series of trans complexes. According to the model, τ_0 for $[RhCl_2(py)_4]Cl$ should be longer than that for the dibromo complex by a factor of about 5. Qualitative observations on the chloro complex indicate a measured lifetime comparable to that of the bromo species ($\tau \simeq 0.5$ msec), but from intensity measurements the efficiency of the chloro complex is estimated to be about $^1/_{10}$th that of the bromo molecule. Thus, τ_0 for the chloro complex is estimated to be about an order of magnitude longer than τ_0 for the bromo complex, definite support for the utility of the model even for the trans molecules.

It is not obvious why the simple spin–orbit-coupling model should work as well as it does. McClure's treatment rests upon the assumption that the energies (relative to the emitting triplet) and absorption intensities of the singlet states from which the spin-forbidden transition gains its allowedness are the same for all the molecules compared. Since the changing of halide substituents in the complexes has a strong effect on the energies of the low-lying charge-transfer states, and since 2,2′-bipyridine and 1,10-phenanthroline have greatly different energy-level schemes and absorption intensities, the fundamental question arises: what type of singlet state is contributing intensity to the emitting triplet? The one type of low-lying state common in all the cis molecules is a d–d singlet. Since spin–orbit coupling is capable of mixing the spin-allowed d-state wave function with any triplet in the cis molecule (ref 30, p 203), it may be reasonable to assume that it is this state from which the triplet acquires its allowedness. One fact supports this conclusion. The lowest d–d spin-allowed band in the *cis*-dichloro complexes is about a factor of 2 weaker than the corresponding band in the dibromo complex. If it is this d–d singlet state which is mixing into the triplet, then, since the energy separation between the singlet and the triplet states is about the same for both molecules, the τ_0 for the chloro complex should be about twice that expected from eq 8 because the latter assumes the same energy gap *and* the same allowedness for the zeroth-order state which mixes with the triplet. Table II shows this prediction to be correct. If this argument is extended to the iodo complexes which have much more intense d–d singlet bands, one would expect measured τ_0's for the iodo complexes to be much shorter than the predicted values in Table II, a contradiction of the facts. Whether the iodo complexes represent a valid test is questionable, as pointed out earlier.[8]

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From consideration of a molecular model for the trans species we conclude that D_4 is the highest symmetry possible. One can therefore argue for the appropriateness of a simple spin–orbit-coupling model to rationalize intensities. The states which mix under spin–orbit coupling are not easy to identify, however. Conceivably charge-transfer or very high-energy excited states are involved in the mechanism.

Kinetics and Mechanism of the Photocyclization of Diphenylamines. I. The Photochemical Primary Processes of Diphenylamines

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Abstract: A kinetic study of the direct, sensitized, and quenched photocyclization of diphenylamines in solution has been carried out. The quantum yields for carbazole formation have been measured in various solvents at 20° spectrophotometrically. On the basis of triplet–triplet energy transfer studied through triplet quenching by the acceptors piperylene and biphenyl and triplet sensitization by the aromatic ketone donors propiophenone, acetophenone, benzaldehyde, etc., photochemical evidence has been presented that photocyclization of diphenylamines occurs through the lowest triplet states of diphenylamines which lead to the formation of an intermediate. The quenching of the quantum yields for product formation by the biacetyl acceptor involved singlet–singlet and triplet–triplet energy transfers. The excess energy requirements, ΔE_T, in these triplet energy transfers were also observed. By means of the steady-state approximation, the photochemical primary processes of *N*-methyldiphenylamine have been revealed in some detail.

Recently, the photocyclizations of *cis*-stilbenes, diphenylamines, and similar organic compounds have been extensively studied. It is well known that the reversible cis–trans photoisomerization of stilbene is accompanied by a photocyclization.[2–8] Mallory and coworkers[9–11] have proposed that the photocyclization of *cis*-stilbene proceeds *via* the 4a,4b-dihydrophenanthrene intermediate whose two central hydrogens are in the trans configuration. Moore, *et al.*,[12] have shown that the intermediate, which has the first absorption band λ_{max} ~450 nm,[13] is transformed into phenanthrene by its oxidation in the presence of oxygen, and back into the ground state of *cis*-stilbene by its thermal decomposition in the degassed solution. Hammond and coworkers[14] have presented photochemical evidence that the intermediate formation occurs from the excited singlet state of *cis*-stilbene. Fischer, *et al.*,[15,16] have reported that the processes of the ring closure and the ring opening in the photocyclization of *cis*-stilbene represent the simplest photochromic system, such as those of spiropyrans and bianthrone-like compounds.[17–20]

The photocyclization of diphenylamines has been reported by several workers in preliminary papers. It was noted by Parker and Barnes that carbazole is a photoproduct of diphenylamine in solution.[21] Bowen and Eland[22] have reported that the photocyclization of diphenylamine involves a different state from the original excited state (but not the triplet, because there is no inhibition by butadiene) and further have found mass spectrometrically that the amount of molecular hydrogen produced is comparable to that of carbazole formed. These results would make us distinguish the status of photocyclization of diphenylamine from that of *cis*-stilbene. However, Linschitz, *et al.*,[23,24] have proposed that, on the basis of flash-excitation studies on N-substituted diphenylamines, the photocyclization of diphenylamines occurs through the triplet state, and the triplet transient converts to another transient, having an

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