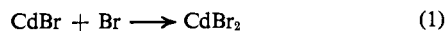cadmium and 3076 Å for zinc, the iodides being slightly shifted toward the visible. A rapid buildup and decay was observed. In the cadmium plus bromine system under conditions producing an excess of bromine atoms, the decay of CdBr was found to be first order in CdBr, corresponding to

$$CdBr + Br \longrightarrow CdBr_2 \qquad (1)$$

Under conditions producing an excess of Cd atoms, the decay was found to be second order in CdBr, corresponding to

$$2CdBr \longrightarrow Cd + CdBr_2 \qquad (2)$$

Extensive studies of the flash photolysis of metal methyl compounds are currently being pursued in this laboratory. A preliminary report on the results obtained with the other compounds will be published shortly.

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Reactions of Hidden n,π* Excited States in N-Heteroaromatics. Photoreduction and Photoaddition[1]

Sir:

N-Heteroaromatic compounds frequently exhibit excited state behavior rather different from their hydrocarbon counterparts. For several nitrogen compounds rapid radiationless decay of initially formed excited singlets evidently competes favorably with fluorescence, intersystem crossing, and chemical reaction.[2-4] Acridine,[5,6] quinoline,[7] and purine[8] undergo photoaddition and photoreduction reactions which appear to involve radical intermediates under conditions where the corresponding hydrocarbons are unreactive. One possibility for explaining this behavior is the involvement of ^{1}n–π* states having radical character and some excitation localization on nitrogen. For excited singlet states of quinoline, acridine, and other large N-heteroaromatics such an explanation seems unappealing; absorption and fluorescence spectra of these compounds show no sign of n → π* transitions and are nearly identical with those of the corresponding hydrocarbons. In addition, studies of acridine indicate that the fluorescent state is a π,π* singlet.[9,10] In the present communication we report novel photoaddition and photoreduction reactions of 1,2-bis(4-pyridyl)ethylene. The results suggest that for this compound, and probably for several

(1) Presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., 1969, Abstract ORGN-16.
(2) J. Lemaire, *J. Phys. Chem.*, **71**, 612 (1967).
(3) B. J. Cohen and L. Goodman, *J. Chem. Phys.*, **46**, 713 (1967).
(4) D. G. Whitten and M. T. McCall, *J. Amer. Chem. Soc.*, **91**, 5097 (1969).
(5) H. Göth, P. Cerutti, and H. Schmid, *Helv. Chim. Acta*, **48**, 1395 (1965).
(6) A. Kira, S. Kato, and M. Koizumi, *Bull. Chem. Soc. Jap.*, **39**, 1221 (1966).
(7) F. R. Stermitz, C. C. Wei, and W. H. Huang, *Chem. Commun.*, 482 (1968).
(8) H. Linschitz and J. S. Connolly, *J. Amer. Chem. Soc.*, **90**, 2979 (1968).
(9) S. J. Ladner and R. S. Becker, *J. Phys. Chem.*, **67**, 2481 (1963).
(10) A. Weller, *Z. Elektrochem.*, **51**, 956 (1957); *Progr. Reaction Kinetics*, **1**, 189 (1961).

other N-heteroaromatics, the presence and reaction of hidden n,π* singlets having lower excitation energies than the initially formed, fluorescent π,π* singlets accounts for many of the unusual photochemical phenomena.

Previously we reported that rapid radiationless decay of excited singlets of 1,2-bis(4-pyridyl)ethylene (**1**) and other nitrogen analogs of stilbene resulted in relatively low efficiencies for *cis–trans* isomerization and fluorescence.[4,11] In benzene the only primary product from direct irradiation of **1** is the *cis* isomer. The lifetime of the excited singlet of **1** in benzene is *ca.* 10^{-12} sec. In other solvent systems we found *cis*-**1** to be the chief product on short-term irradiation; however irradiation of **1** in methylcyclohexane and 2-propanol leads to the formation of additional products with low quantum efficiencies. These products, which build up gradually at the expense of **1**, proved to be substituted 1,2-bis(4-pyridyl)ethanes formed by addition of hydrogen or solvent across the acyclic double bond (eq 1).
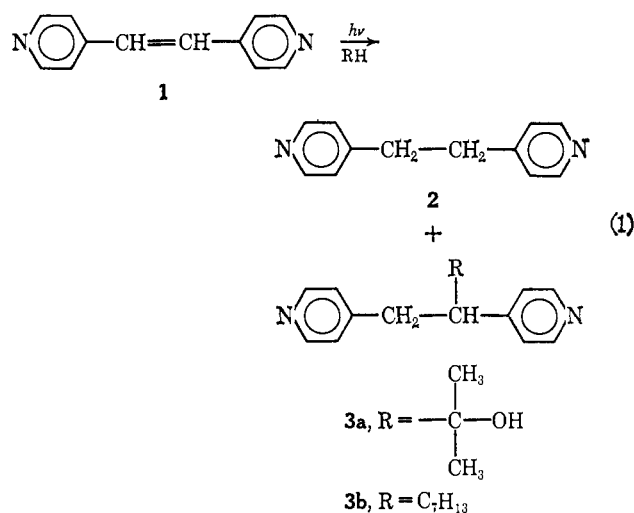
In a typical experiment irradiation of **1** in 2-propanol led to a 21% yield of **2** and a 28% yield of **3a**. Long-term irradiation of **1** in methylcyclohexane yields **2** and **3b**. Although **2** is not produced initially by irradiation of **1** in benzene, long-term irradiation leads to slow formation of roughly equal quantities of 3,6-diazaphenanthrene and **2**. Quantum efficiencies for formation of **2** and *cis*-**1** are listed in Table I.

Table I. Initial Quantum Efficiencies for Photoreduction and Isomerization of 1,2-Bis(4-pyridyl)ethylene

|	Benzene	Methyl-cyclohexane	2-Propanol	Water-acetonitrile[b]
$\phi_{t \rightarrow c}$	0.003	0.005	0.04	0.3
$\phi_{t \rightarrow 2}$	0.0	0.0004	0.02	

a Degassed solutions, irradiated at 313 nm, olefin concentration 0.005 *M*. *b* 70% acetonitrile by volume.

The surprising observation of photoaddition and photoreduction reactions for an acyclic olefin such as **1** raises several questions regarding mechanism. It appears that products **2** and **3** arise from solvent hydrogen

(11) D. G. Whitten and M. T. McCall, *Tetrahedron Lett.*, 2755 (1968).

abstraction by excited **1** and subsequent reaction (addition or hydrogen abstraction) of the intermediate radical. Stilbene does not participate in analogous reactions; a mechanism involving direct hydrogen abstraction by an ethylenic carbon is rather unattractive. By analogy with photoreactions of other N-heterocyclic compounds[6,8,12] we suggest formation of **2** and **3** involves hydrogen abstraction by nitrogen and subsequent rearrangement of the initial product (eq 2).
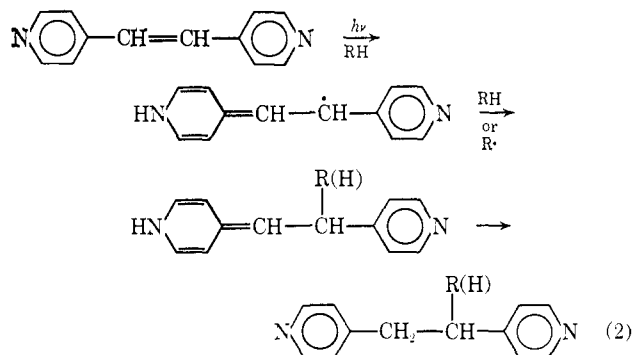
Excited triplets of **1** are evidently not involved in formation of **2** and **3**; irradiation of 2-propanol or methylcyclohexane solutions containing sensitizers such as triphenylene or Michler's ketone and **1** leads only to *cis–trans* isomerization even on very long-term irradiation. The question of singlet participation in the reaction is less easily resolved. Absorption spectra of **1** are nearly identical in all the solvents listed in Table I. In principle, comparison of quantum efficiencies for reduction, fluorescence, and isomerization of **1** in the presence and absence of hydrogen atom donors should enable determination of the excited states responsible for each process. Although the efficiency of reduction of **1** in methylcyclohexane appears too low for it to show competition with fluorescence and intersystem crossing, the actual efficiency of initial hydrogen abstraction is probably much higher. In fact, fluorescence and isomerization efficiencies are essentially unchanged by changing solvent from benzene to methylcyclohexane. In 2-propanol and acetonitrile–water the weak fluorescence of **1** is very slightly enhanced over that in benzene. Isomerization efficiencies increase markedly when the solvent is changed from the hydrocarbons to 2-propanol or acetonitrile–water. The most significant aspect of these findings is that both isomerization and reduction are uncoupled from fluorescence; each of these processes apparently originates from some later-obtained state. A tempting possibility is that the lifetime of the fluorescent (π,π^*) singlet of **1** is shortened by rapid internal conversion to a lower n,π^* singlet. We suggest that photoreduction and photoaddition occur *via* hydrogen abstraction by this n,π^* singlet and that isomerization occurs from the triplet.[13] If n,π^* singlets are hidden due to their extremely weak oscillator strength, it is reasonable that in the absence of hydrogen

(12) F. R. Stermitz and C. C. Wei, *J. Amer. Chem. Soc.*, **91**, 3103 (1969).
(13) Although other explanations could be advanced, a possible explanation for the enhanced isomerization efficiency is that increases in energy of the ^{1}n,π^* state in polar solvents facilitate rapid ^{1}n,π^* $\rightarrow$ $^3\pi,\pi^*$ intersystem crossing.[14] Interestingly, CNDO-II molecular orbital calculations[15] suggest that lowest excited states of **1** are n,π^*.
(14) See, for example, M. A. El-Sayed, *Accounts Chem. Res.*, **1**, 8 (1968).
(15) L. G. Pederson, D. G. Whitten, and M. T. McCall, *Chem. Phys. Lett.*, **3**, 569 (1969).

atom donors they should decay nonradiatively to the ground state.

Attempts to determine whether hidden n,π^* singlets are a general phenomenon for other N-heteroaromatics are in progress. Recent studies[16] indicate that the photoreduction of acridine does not originate from either the fluorescent (π,π^*) singlet or the triplet; here again a hidden ^{1}n,π^* state is the probable reactant.[17]

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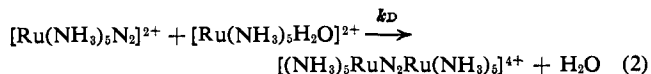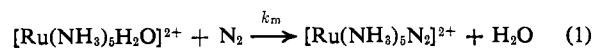## Heat of Nitrogen Binding with Ruthenium(II)–Ammine Complexes

Sir:

The discovery[1] of $[Ru(NH_3)_5N_2]^{2+}$ and $[(H_3N)_5RuN_2Ru(NH_3)_5]^{4+}$ and the remarkable stability of these ions have prompted a number of recent investigations.[2-4] The enthalpy of coordination of N_2 should provide some insight into the nature of interaction of molecular nitrogen with ruthenium.

Solutions of $[Ru(NH_3)_5H_2O]^{2+}$ ranging in concentration from 0.1 to 0.03 M were prepared by the reduction of $[Ru(NH_3)_5Cl]^{2+}$ with zinc amalgam in 0.1 M H_2SO_4 under an atmosphere of argon. The $[Ru(NH_3)_5Cl]Cl_2$ was prepared from commercial anhydrous $RuCl_3$ by a slight modification of the method of Allen, *et al.*[5] One gram of $RuCl_3$ was dissolved in 12 ml of H_2O, 10 ml of $N_2H_4\cdot H_2O$ (85%) was added, and the mixture was stirred for 1 hr. The mixture was then refluxed for 1 hr, allowed to stand overnight, and filtered by gravity; then 10 ml of 6 N HCl was added to the filtrate. This solution was refluxed for 1 hr and the $[Ru(NH_3)_5Cl]Cl_2$ was removed by filtration, washed, and dried.

The addition of nitrogen to $[Ru(NH_3)_5H_2O]^{2+}$ was followed in a gas reaction microcalorimeter[6] by adding N_2 to a solution of $[Ru(NH_3)_5H_2O]^{2+}$ in 0.1 M H_2SO_4. The formation of $[Ru(NH_3)_5N_2]^{2+}$ and $[Ru(NH_3)_5N_2(NH_3)_5Ru]^{4+}$ was confirmed spectrally. The calorimeter used was capable of measuring heats of a few millicalories attending the uptake of a few micromoles of N_2, as followed manometrically.[6]

The heat per mole of N_2 uptake is due to a possible combination of two reactions.

$$[Ru(NH_3)_5H_2O]^{2+} + N_2 \xrightarrow{k_m} [Ru(NH_3)_5N_2]^{2+} + H_2O \quad (1)$$

$$[Ru(NH_3)_5N_2]^{2+} + [Ru(NH_3)_5H_2O]^{2+} \xrightarrow{k_D}$$
$$[(NH_3)_5RuN_2Ru(NH_3)_5]^{4+} + H_2O \quad (2)$$

Both of these reactions have been followed kinetically[3] with rate constants determined at 20° as $k_m = 4.4$

(1) A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1965).
(2) D. F. Harrison, E. Weissberger, and H. Taube, *Science*, **159**, 320 (1968).
(3) I. S. Itzkovitch and J. A. Page, *Can. J. Chem.*, **46**, 2743 (1968).
(4) D. E. Harrison and H. Taube, *J. Amer. Chem. Soc.*, **89**, 2706 (1967).
(5) A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *ibid.*, **89**, 5595 (1967).
(6) S. Boyle, M. S. Thesis, University of Colorado, 1969.