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Photochemical and Thermal Behaviour of Isocyanide Complexes
I. A Kinetic Study of the $Fe(bpy)_2(CNCH_3)_2^{++}$–Hydrazine Reaction

L. L. COSTANZO, S. GIUFFRIDA, G. DE GUIDI and S. PISTARA'

Istituto Dipartimentale di Chimica e Chimica Industriale dell'Università, Viale A. Doria 8, 95125 Catania, Italy

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The thermal reaction between $Fe(bpy)_2(CNCH_3)_2^{++}$ (bpy is 2,2'-bipyridyl) and hydrazine in acetonitrile led to a dicarbene complex, that in the presence of hydrazine underwent a reversible deprotonation equilibrium $K = 8.4 \cdot 10^{-4}$. The dicarbene complex formation occurred according to the rate law $k_{obs} = k$ [hydrazine]. The activation parameters were $\Delta H^{\neq} = 57 \pm 3$ KJ (M^{-1}); $\Delta S^{\neq} = -145 \pm 7$ J(M^{-1} K^{-1}).

The proposed mechanism suggests that the reaction occurs through a first slow step, involving a concerted attack on the CN of an isocyanide by the NH of the hydrazine, followed by a second fast NH–CN attack with ring closure.

Introduction

In the course of our investigation of the photochemical behaviour of isocyanide complexes in aprotic solvents, we examined the isocyanide–hydrazine photosubstitution in $Fe(bpy)_2(CNCH_3)_2^{++}$ [1]. Because the hydrazine is a ligand able to undergo thermal addition to two adjacent isocyanides to yield a chelating carbene ligand [2, 3], we considered that a preliminary study of the thermal reaction $Fe(bpy)_2(CNCH_3)_2^{++}$–hydrazine was useful to establish the conditions suitable for incurring no interference between photochemical and thermal processes. In this paper we report the results of the kinetics of the dicarbene compound $Fe(bpy)_2(C_4H_{10}N_4)^{++}$ formation in acetonitrile.

Experimental

Preparation of Compounds

The *cis*-$[Fe(bpy)_2(CNCH_3)_2](BF_4)_2$ was prepared by treating $Fe(bpy)_2(CN)_2 \cdot 2H_2O$ with a slight excess of $(CH_3)_2SO_4$ according to the method reported earlier [4]. The product was precipitated with a saturated aqueous solution of $NaBF_4$ and purified by recrystallization from acetonitrile–n-propanol.

The $[Fe(bpy)_2(C_4H_{10}N_4)](BF_4)_2$ was prepared by refluxing a solution of $[Fe(bpy)_2(CNCH_3)_2](BF_4)_2$ (600 mg) and hydrazine (0.75 ml) in 20 ml of acetonitrile at 50 °C for 5 hours, using a procedure analogous to that described for $[Fe(o\text{-phen})_2(C_4H_{10}N_4)](BF_4)_2$ [2].

The analytical data and IR and NMR spectra were consistent with those expected: *Anal.* Calcd: C, 43.94; H, 3.99; N, 17.08. Found: C, 43.71; H, 4.02; N, 16.95. IR (cm^{-1}): 3420 and 3300 (ν_{NH}); 3060 and 2920 (ν_{CH}); 1470 and 1440 ($\nu_{N \cdots C \cdots N}$). All stretching frequencies of the 2,2'-bipyridyl were present. NMR (CD_3CN, 60 MHz): 2.96 (d, 6H, J = 5 Hz), 5.92 (m, 2H), 7.1–8.6 (m, 16H), 9.87 (m, 2H).

Materials

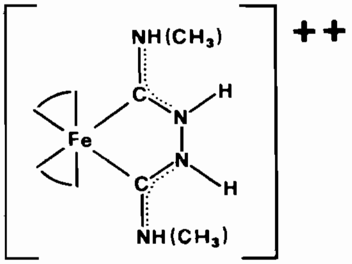
Acetonitrile (RS C. ERBA) and hydrazine hydrate (C. ERBA) were used.

Apparatus

The IR spectra were recorded on a Perkin-Elmer Mod. 257 spectrophotometer as KBr pellets and the NMR spectra on a Varian EM 360 instrument in acetonitrile-D_3, using TMS as internal standard. All UV spectra and kinetic data were obtained using an Optica CF_4 spectrophotometer with the cell compartment thermostatted at the desired temperature.

Results and Discussion

The addition of hydrazine to two isocyanide ligands of $Fe(bpy)_2(CNCH_3)_2^{++}$ (*I*) yielded a violet cation (*II*) which has been isolated as tetrafluoroborate salt.



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The absorption spectra of (*II*) in CH_3CN show two intense band systems in the visible region at 560 and 520 nm (ϵ 5,800 and 5,200) and at 370 nm (ϵ 6,900), which can be attributed to charge transfer transitions of metal-ligand type. The shifts of these bands to wavelengths longer than the isocyanide parent support the assumption that the dicarbene ligand was a poorer π-acceptor and stronger σ-donor than the two isocyanides [2]. In the UV region the bands at 300 nm (ϵ 38,500) and 245 nm (ϵ 25,000), attributed to IL transitions, were almost unchanged (Fig. 1).

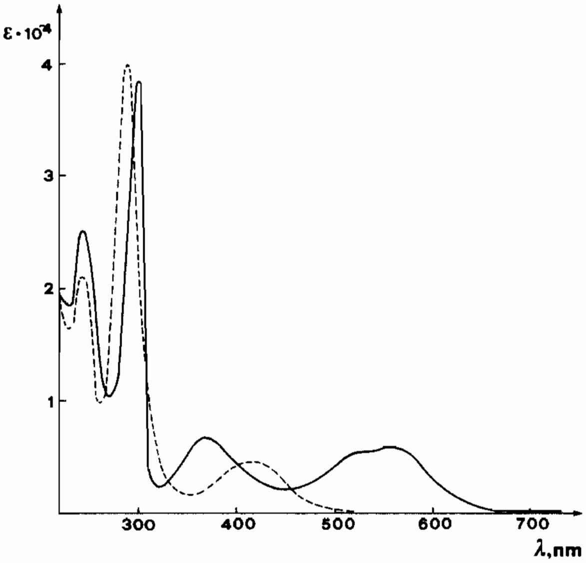

Fig. 1. Absorption spectra of $Fe(bpy)_2(CNCH_3)_2^{++}$ (-----) and of $Fe(bpy)_2(C_4H_{10}N_4)^{++}$ (——) in acetonitrile.

Compound (*II*) in the presence of a base as hydrazine underwent a reversible reaction of deprotonation with the formation of a dark-green monocationic species:

$$\underset{(II)}{Fe(bpy)_2(C_4H_{10}N_4)^{++}} + N_2H_4 \rightleftharpoons \underset{(III)}{Fe(bpy)_2(C_4H_9N_4)^{+}} + N_2H_5^{+} \qquad (1)$$

The starting compound can be regenerated by treatment with acid. This equilibrium was attributed to acidic properties of the carbene ligands [3, 5], which can lose a proton from one of the interior nitrogen atoms of the chelate ring.

The deprotonation equilibrium (1) was evidenced through the variation of the visible absorption spectra of the dicarbene compound at the various hydrazine concentrations (Fig. 2). Three constant isosbestic points ensure that there was equilibrium only between the two forms (*II*) and (*III*). In large hydrazine excess ([hydrazine]/[compound] $\approx 10^4$) the spectrum was practically insensitive to further additions of base; in these conditions we considered the carbene compound to be entirely in the deprotonated form (*III*). The spectrum of the monocationic species (III) showed charge transfer bands at 680 nm (ϵ 6,200), 580 nm (ϵ 4,200) and 420 nm (ϵ 8,900). The lower energies of these bands compared with those of non-deprotonated species (*II*) were ascribed to a decreasing ability of the deprotonated dicarbene ligand to favour π backdonation. Attempts to isolate the deprotonated species have not been successful.

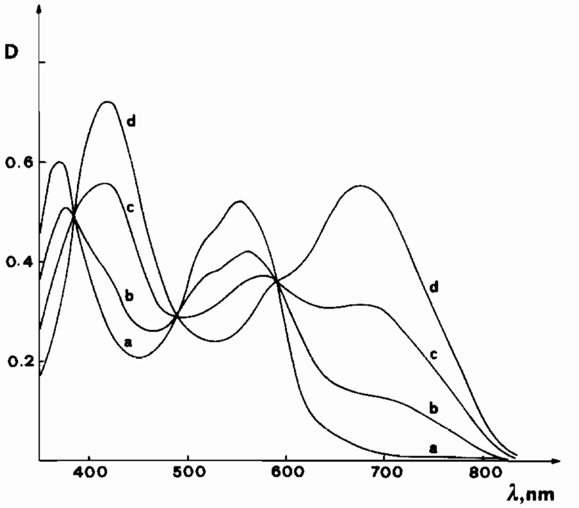

Fig. 2. Changes of absorption spectra of $Fe(bpy)_2(C_4H_{10}N_4)^{++}$ ($0.86 \cdot 10^{-4}$ *M*) at various concentrations of hydrazine. $[N_2H_4]$ = 0 (a); 10^{-2} *M* (b); $8 \cdot 10^{-2}$ *M* (c); 1.5 *M* (d).

From the spectrophotometric data we deduced the equilibrium constant $K = 8.4 \cdot 10^{-4}$ (error < 8%), that was independent of temperature in the range 25–40 °C.

The kinetics of dicarbene compound formation have been studied at various temperatures with substrate concentration in the range $0.5–1.2 \cdot 10^{-3}$ *M* in excess of hydrazine in order to yield kinetics of pseudo first order. In these conditions the dicarbene compound was obtained in a deprotonated form (*III*). Kinetic data have been deduced from the appearance of the dicarbene compound, both at 680 nm, absorption maximum, and at 490 nm, isosbestic point of (*II*) and (*III*). In both cases similar data were obtained, and this confirmed that the equilibrium reaction (1) was a fast process. As expected, the reaction was of pseudo first order and the rate was a function of the hydrazine concentration.

$$\frac{d[Fe(bpy)_2(C_4H_9N_4)^+]}{dt} = k_{obs}[Fe(bpy)_2(CNCH_3)_2^{++}]$$

From plots of the rate constants k_{obs} versus hydrazine concentration, straight lines were obtained at various temperatures (Fig. 3).

The observed linear dependence was in accordance with the kinetic law:

$k_{obs} = k[N_2H_4]$

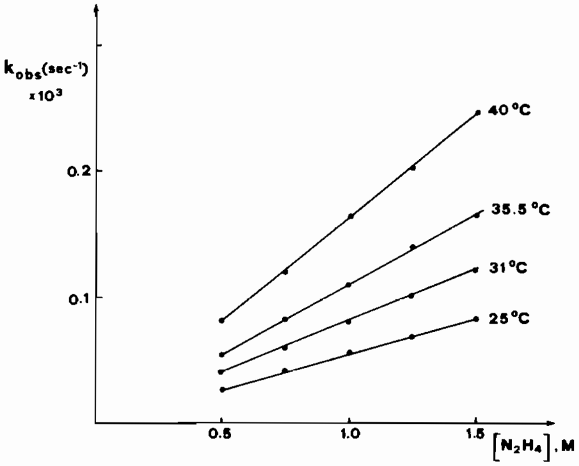

Fig. 3. Dependence of k_{obs} on hydrazine concentrations.

TABLE I. Kinetic Data for $Fe(bpy)_2(C_4H_{10}N_4)^{++}$ Formation.[a]

$k \cdot 10^3$ (M^{-1} sec^{-1})	t (°C)
0.055	25
0.082	31
0.11	35.5
0.16	40

[a] $\Delta H^{\neq} = 57 \pm 3$ KJ (M^{-1}); $\Delta S^{\neq} = -145 \pm 7$ J (M^{-1} K^{-1}).

The k values and the activation parameters are summarized in Table I.

The same kinetic law was found previously for the formation of monocarbene complexes from square planar Pd and Pt compounds in aprotic solvents [6–7], and in the case of dicarbene complex formation from $Fe(CNCH_3)_6^{++}$ in aqueous solution [8]. Given this analogy, we suggest for the case under study a reaction mechanism involving a slow first step, determining the rate, followed by a fast second step. In the first step a concerted attack on the C and N of an isocyanide by the N and H of hydrazine can occur, with the formation of an activated complex at four centers. The high negative value of the entropy is consistent with the hypothesis of a transition state involving a rigid structure with reduction of degrees of freedom. In the first step a monocarbene complex was yielded, but in the octahedral configuration the free NH_2 group of hydrazine has no place apart from the second isocyanide; consequently, a fast step involving a further NH–CN attack with ring closure and dicarbene complex formation is expected. In this mechanism it is reasonable to find lower rates of reaction compared with those for square planar compounds: in fact, the octahedral geometry and the presence of two bipyridyl rings makes it more difficult to penetrate and modify the coordination sphere. On the other hand, this steric hindrance would facilitate a rapid ring closure and give the observed dicarbene.

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