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Kinetics of Thermal and Photochemical Decomposition of *cis*- and *trans*-Dicyanotetrakis(methylisocyanide)iron(II)

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Thermal and photochemical kinetic studies of cis- *and* trans-$Fe(CNCH_3)_4(CN)_2$ *are reported and discussed. The UV spectra are determined and the charge transfer and* d-d *bands assigned. In alkaline buffer medium both compounds decompose to* Fe^{2+} *and free ligands. The reaction is first-order in* $[OH^-]$ *and first-order in [complex]. The activation energy and entropy are calculated. The kinetics may be explained by an* S_N2 *mechanism with nucleophilic attack by hydroxide ion. The excitation of aqueous solutions of both isomers with 254,280 and 313 nm radiations, corresponding to charge transfer and ligand field bands, promotes substitution reactions of* $CNCH_3$ *by* H_2O*. The quantum yield values for the formation of diaquo-compounds are determined and the photoaquation reaction mechanism discussed.*

Introduction

In earlier studies, the thermal and photochemical behaviour of isocyanide complexes [$Fe(CNCH_3)_6^{2+}$,[1] $Fe(AA)_2(CNCH_3)_2^{2+}$,[2] and $Fe(AA)(CNCH_3)_4^{2+}$ [3] (AA = 1,10-phenanthroline or 2,2'-bipyridine)] were investigated in solution. The interesting results obtained have encouraged an extension of the study to dicyanotetrakis(methylisocyanide)iron(II) which also offers the possibility of comparing the kinetic and photochemical properties of *cis*- and *trans*-isomers. The crystal structures[4] of both isomers, prepared in a high state of purity, are known. Moreover Mössbauer[5] and vibrational[6] spectra have revealed that the metal-ligand bond strength is not greatly dependent on the nature of the ligand *trans* to a given bond, and that the extent of π delocalisation is much the same for both types of ligand.

This paper reports the results of a study on the base hydrolysis and the direct photolysis of *cis*- and *trans*-$Fe(CNCH_3)_4(CN)_2$.

Experimental Section

Materials. *cis*- and *trans*-$Fe(CNCH_3)_4(CN)_2$ were prepared[7] by heating $Fe(CNCH_3)_6Cl_2$ under vacuum for 10 hr. at 150°. The isomers were separated and purified according to the procedure recommended by Berrett and Fitzsimmons.[5] The reaction mixture was extracted with hot chloroform and the extract cromatographed on alumina column. The *trans*-isomer (Found: C, 44.5; H, 4.7; N, 30.6; Fe, 20.2) was eluted with chloroform, and the *cis*-isomer (Found: C, 44.7; H, 4.6; N, 30.1; Fe, 20.4. Calcd for $C_{10}H_{12}FeN_6$: C, 44.1; H, 4.4; N, 30.9; Fe, 20.5) with chloroform-methanol (1:1), and they were recrystallised from methanol and chloroform, respectively. Purity was finally checked by thin layer chromatography. The two isomers were easily distinguished by their IR spectra in the region of the cyano stretching vibrations; the isocyanoband has two peaks in the *cis*- and one in the *trans*-isomer. Deionized water and reagent grade chemicals were used in all procedures.

Thermal Kinetic Measurements. All kinetic studies were carried out in water solutions at regulated temperatures (±0.1). The complex concentrations were in the range 5.10^{-4} to 10^{-3} *M*. The base hydrolysis was carried out at 60, 65, 70, 75, 80 and 85°, in buffer solutions (Sorensen's borate mixtures). The compounds decompose in to Fe^{2+} and free ligands; the kinetics of the decomposition were studied in presence of excess phenanthroline to complex the released Fe^{2+} and to determine the later as $Fe(phen)_3^{2+}$ by spectrophotometric method at 510 nm. The determination is not disturbed by the presence of $Fe(CNCH_3)_4(CN)_2$, phen, CN^- and $CNCH_3$. The phenanthroline does not affect the kinetics of decomposition, as proved by the results obtained at various concentrations of phenanthroline. The kinetic measurements were carried out until a small percentage (10 per cent) of the initial compound was decomposed, in order to avoid the formation of too many CN^- ions, which might form $Fe(CN)_6^{4-}$ in competition to $Fe(phen)_3^{2+}$. In addition, the kinetic salt effect was investigated by adding NaCl, KCl, Na_2SO_4 to the reaction mixture (maximum value of ionic strength, 0.5 *M*).

Photochemical Apparatus and Procedures. The irradiation equipment consists of a source, filters, diaphragm and reaction cell, all in line along an optical

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(1) V. Carassiti, G. Condorelli, and L.L. Condorelli Costanzo, *Ann. Chim. Rome, 55,* 329 (1965).

(2) G. Condorelli and L.L. Condorelli Costanzo, *Ann. Chim. Rome,* 56, 1140 (1966).

(3) G. Condorelli and L.L. Condorelli Costanzo, *Ann. Chim. Rome,* 56, 1159 (1966).

(4) H.M. Powell and G.B. Stanger, *J. Chem. Soc.,* 1105 (1939); R. Hume and H.M. Powell, *J. Chem. Soc.,* 719 (1957).

(5) R.R. Berrett and B.W. Fitzsimmons, *Chem. Comm., 91* (1966); *J. Chem. Soc. (A),* 525 (1967).

(6) R.R. Berrett, B.W. Fitzsimmons, P. Gans, H.M.N.H. Irving, and P. Stratton, *J. Chem. Soc. (A),* 904 (1969).

(7) E.G.J. Hartley, *J. Chem. Soc., 103,* 1195 (1913).

axis. The light of required wavelengths was isolated as follows: 254 nm - Source: Hanau NN 15/44 low-pressure mercury vapour lamp; filter:[8] 2 cm of a solution containing 321 g of $NiSO_4 . 7H_2O$ and 56 g of $CoSO_4 . 7H_2O/1$. Extraneous transmission (4%) was between 297 and 313 nm. 280 nm - Source: Hanau Q81 mercury vapor lamp; interference filter: Ealing TFP, $\lambda_{max} = 280$ nm, $T_{max} = 18.5\%$, halfwidth = 14 nm. 313 nm - Source: Hanau Q 400 mercury vapor lamp; filter: 1 cm of 0.02% solution of K_2CrO_4 in 0.05 N NaOH + 2 mm of Chance glass OX 1. Extraneous transmission (13%) was between 302 and 366 nm. The reaction cells were standard 10 nm spectrophotometer cells. The light beam was sufficiently collimated and the solution absorption such that all incident light was contained by the irradiated solution. In order to avoid secondary photoreactions, only a small per cent of the initial complex concentration was decomposed.

During irradiation, the cells were kept at 10° and the solutions were stirred by bubbling pure nitrogen through a glass capillary. Light intensity measurements were made by means of the ferric oxalate actinometer.[8] The incident light intensities were always of the order of 10^{-7} einstein/min.

Spectrophotometric measurements were carried out with an Optica CF4NI spectrophotometer.

Results and Discussion

Electronic Spectra. The spectra of the two compounds, reported in Table I, show two unresolved bands, which may be assigned[9] to spin-allowed but Laporte-forbidden *d-d* transitions from the ground state $^1A_{1g}$ to the $^1T_{1g}$ and $^1T_{2g}$ excited states. There is also a high intensity band which may be assigned[9] to C.T. from the metal to the ligand orbitals. The lower ε values for *trans*-$Fe(CNCH_3)_4(CN)_2$ are consistent with a centrosymmetrical configuration. The two expected bands to spin-forbidden singlet-triplet transitions were not observed.

Table I. Electronic Spectra in Aqueous Solution.

	nm	ε	Assign.
cis-$Fe(CNCH_3)_4(CN)_2$	315	360	*d-d*
	(265)	460	*d-d*
	210	22.000	*d-d*
trans-$Fe(CNCH_3)_4(CN)_2$	315	330	*d-d*
	(265)	410	C.T.
	210	21.000	C.T.

Base Hydrolysis. Under the hydrolysis conditions described in the previous section, *cis*- and *trans*-$Fe(CNCH_3)_4(CN)_2$ complexes decompose following a pseudo-first-order kinetic.

Observed first-order rate constants (k_{obs}) are reported in Table II. In all case, plots of k_{obs} against hydroxide ion concentration are linear; the plots pass through the origin within the experimental uncertainty. Typical k_{obs} against $[OH^-]$ plots are shown in the Figure 1.

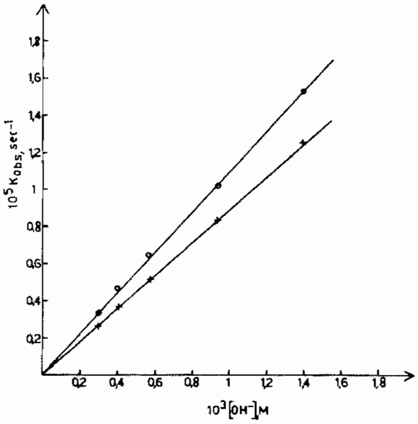

Figure 1. The dependence of observed first-order rate constants(k_{obs}) on hydroxide concentration for *cis* (-o-o-o-) and *trans*$Fe(CNCH_3)_4(CN)_2$(-x-x-) Temperature 85°C.

The general rate law of the reaction is thus:

$$-d[Fe(CNCH_3)_4(CN)_2]/dt = k[OH][Fe(CNCH_3)_4(CN)_2] \quad (1)$$

From the observed first-order rate constants, second-order constants k, as defined by equation (1), were determined graphically; their values are also included in Table II. The activation energy for the base hydrolysis reaction of the *cis*- and *trans*-isomers, calculated between 60 and 85°, is 28 ± 1 and 31 ± 1 Kcal, respectively. The activation entropy at 80° is 5.8 and 17.6 e.u., respectively.

The values of the kinetic constants are independent of the ionic strength: this proves that a nonionic species is involved in the rate-determining step.

By considering the involvement of OH^- in the rate expression alone, it is not possible to distinguish between the associative or dissociative mechanism. However, the observed low values for the second-order rate constants and the absence of acid protons in the complexes lead one to accept the simpler mechanism S_N2.. The hydroxide ion attack may occur between the π orbitals of the nucleophilic and the antibonding orbital of the metal, with resultant destabilization of the metal-ligand bonds and subsequent dissociation of the complex.

Photochemical Behaviour. Irradiation of *cis*- and *trans*-$Fe(CNCH_3)_4(CN)_2$ at 254,280 and 313 nm leads to a change in the spectra of aqueous or acid (pH 2-6) solutions of these complexes. (In the dark the original solutions are kinetically stable).

One can note in Figure 2 the regular variation of absorption with the irradiation time and the appearance of a band at 415 nm, where the absorption of the original complex is negligible.

The isosbestic points at 298 and 345, at 298 and

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(8) C.G. Hatchard and C.A. Parker, *Proc. Roy Soc.*, *A235*, 518 (1956).

(9) The excited states assignments are related to previous assignments made for $Fe(CNCH_3)_6^{2+}$ and $Fe(CN)_6^{4-}$ (P.C. Fantucci, V. Valenti and F. Cariati, *Inorg. Chim. Acta*, *5*, 425 (1971); J.J. Alexander and H.B. Gray, *J. Am. Chem. Soc.*, *90*, 4260 (1968)).

Table II. Observed first-order constants (k_{obs}) and derived second-order rate constants k for hydroxide attack at *cis*- and *trans*-$Fe(CNCH_3)_4(CN)_2$ complexes, at various temperatures, ionic strength 0.1 *M*.

		10^5k_{obs},sec^{-1}					
		$10^3\lvert OH^-\rvert$,*M*					
	Temp.,C	0.30	0.42	0.58	0.94	1.40	10^2k
cis-$Fe(CNCH_3)_4(CN)_2$	60	0.012	0.017	0.024	0.039	0.058	0.042
	65	0.025	0.035	0.048	0.078	0.116	0.083
	70	0.050	0.068	0.095	0.152	0.228	0.166
	75	0.098	0.130	0.180	0.288	0.420	0.312
	80	0.167	0.225	0.315	0.510	0.760	0.543
	85	0.340	0.460	0.638	1.022	1.530	1.097
trans-$Fe(CNCH_3)_4(CN)_2$	60	0.009	0.013	0.018	0.030	0.044	0.032
	65	0.019	0.026	0.037	0.059	0.089	0.064
	70	0.035	0.050	0.070	0.115	0.170	0.125
	75	0.073	0.100	0.140	0.230	0.340	0.245
	80	0.130	0.183	0.258	0.420	0.630	0.445
	85	0.265	0.365	0.513	0.835	1.245	0.875

343 are present for *cis* and *trans* isomers, respectively.

During irradiation only production of $CNCH_3$ has been observed. When $CNCH_3$ was added to irradiated solutions so as to give a 0.5 *M* concentration, the spectrum came back to the "zero-time" dark values. These observations indicated that the photochemical process is an aquation reaction where $CNCH_3$ molecules are replaced by H_2O. The constancy of the isosbestic points for relatively short periods leads one to believe that only one photoproduct is formed, at least initially.

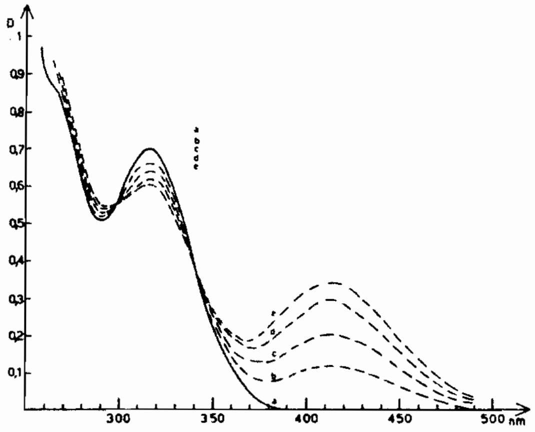

Figure 2. Spectral change for a $1.9\times10^{-4}M$ aqueous solution of *cis*-$Fe(CNCH_3)_4(CN)_2$, irradiated with 313 nm light; a,b,c,d,e are the spectra recorded after 0,5,10,15,18 min of irradiation, respectively.

The concentration of the aquo-complex present in an irradiated solution was determined by decomposition of same at 60°, and subsequent determination of released Fe^{2+} as $Fe(phen)_3^{2+}$. (Under the experimental conditions used the initial complex does not decompose). The concentration values obtained and the optical density measurements above 400 nm allowed, in combination with the data of Figure 2, a calculation of the complete spectrum of the aquo-complex. The electronic absorption spectra of the aquo complexes, compared to those of *cis*- and *trans*-$Fe(CNCH_3)_4(CN)_2$, are shown in Figures 3, 4. The spectra present the same type of bands as those of the original compounds, but shifted to a longer wavelength because of the replacement of $CNCH_3$ by H_2O. (The high intensity of the band at 413 nm is attributed to elevated distorsion, caused by three types of ligands).

Accepting Tsuchida's rule of *average environment*, in which the wave number of the Laporte-forbidden bands of a mixed-ligand complex are approximately

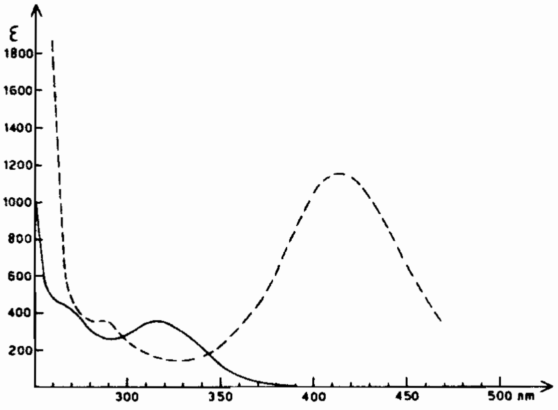

Figure 3. Absorption spectra of *cis*-$Fe(CNCH_3)_4(CN)_2$(——) and diaquocomplex (----) in aqueous solution at 10°C.

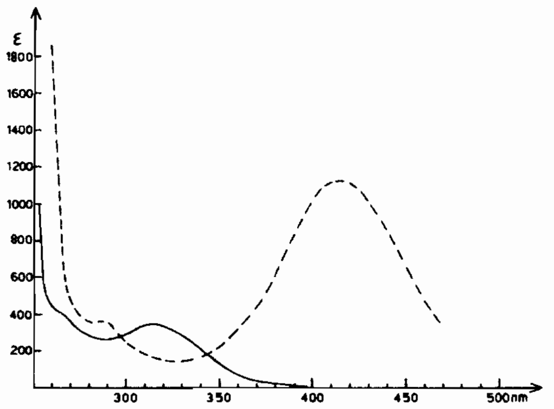

Figure 4. Absorption spectra of *trans*-$Fe(CNCH_3)_4(CN)_2$ (——) and diaquocomplex (----) in aqueous solution at 10°C.

obtained by interpolating the wave numbers of the pure complexes, the position of the band at 413 nm is in accordance with the presence of 2 molecules of H_2O, CN^- and $CNCH_3$, respectively. Therefore the photolysis products may be diaquo-compounds, $Fe(CNCH_3)_2(H_2O)_2(CN)_2$.

The appearance of $Fe(CNCH_3)_2(H_2O)_2(CN)_2$ as the first observed product may be explained on the basis that a fast thermal aquation of the immediate photoproduct $Fe(CNCH_3)_3(H_2O)(CN)_2$ occurs:

$$Fe(CNCH_3)_4(CN)_2 \xrightarrow{h\nu} Fe(CNCH_3)_3(H_2O)(CN)_2 + CNCH_3$$

$$Fe(CNCH_3)_3(H_2O)(CN)_2 \overset{fast}{\leftrightarrows} Fe(CNCH_3)_2(H_2O)_2(CN)_2 + CNCH_3$$

It is unlikely that simultaneous aquation of two isocyano groups occurs in the primary step.

Quantum Yield. The formation of the aquoproducts by irradiation of *cis*- and *trans*-$Fe(CNCH_3)_4(CN)_2$ at 254,280 and 313 nm, was followed spectrophotometrically at 415 nm. The concentration of $Fe(CNCH_3)_2(H_2O)_2(CN)_2$ increases linearly with irradiation time (zero-time reaction).

The quantum yields were found independent of the exciting wavelength; the values are for

cis-$Fe(CNCH_3)_4(CN)_2$ $\Phi = 0.14 \pm 0.05$

trans-$Fe(CNCH_3)_4(CN)_2$ $\Phi = 0.13 \pm 0.05$

The wavelengths used for irradiation correspond to C.T. band (254 nm) and to singlet ligand field bands (280 and 313 nm). In spite of the difference in energy and also in nature among the various excited states reached by irradiation, the same type of photoreaction and the same quantum yields were always obtained.

These results suggested that rapid radiationless transitions of unitary efficiency led the higher excited states to the lowest one (i.e. to a triplet ligand field state[10]) which could be the precursor of the photoaquation having a quantum yield equal to 0.14 and 0.13 for the two isomers.

This photoaquation reaction, however, might also take place in vibrational excited levels of the ground state, reached by an intersystem crossing from the lowest triplet state.

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(10) Preliminary results obtained on sensitized photoaquation are accordance with this mechanism.