A Kinetic Study of the Formation of Carbene Complexes from the Reaction between Hexakismethylisonitriloferrate(II) and some Nitrogenous Bases in Aqueous Solution

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The formation of the product containing a chelating dicarbene, formed by the attack of hydrazine on the hexakismethylisonitriloferrate(II) complex, is first order in each reagent, independent of ionic strength but varies with hydrogen ion concentration. While attack by methylhydrazine shows similar kinetic features, the behaviour when methylamine is used as the nucleophile is different. Rate data are presented and a mechanism suggested for the reactions involved.

Introduction

The formation of complexes containing carbene ligands, by the attack of bases on co-ordinated isonitriles, is well documented, especially in the cases of square-planar d^8 complexes [1–4] and octahedral d^6 complexes [5–9]. In this paper we report the results of kinetic studies of such reactions. Specifically the attack of hydrazine, methylhydrazine and methylamine on the hexakis-methylisonitriloiron(II) ion in aqueous solution. These studies are intended to augment those already reported for d^8 systems [10, 11]. There are clear differences between the reactions of the two groups of complexes. These are illustrated by the relative rates of reaction, and the ease of formation of chelated di-carbene ligands as distinct from monodentate carbenes.

Results and Discussion

All the reactions discussed here were studied in aqueous media, since both the hexakis-methyliso-nitriloiron(II) complex reagent and the methylisonitrilodicarbenoiron(II) products are soluble as the bisulphates. Preliminary studies showed that, for dilute solutions, the ultra-violet spectra of reagent and products obey the Beer–Lambert law, and that the products show a much greater absorbance between 240 and 260 nm than does the reagent. The reactions with hydrazine and methylhydrazine were followed at 250 nm, while that with methylamine was followed at 240 nm, wavelengths at which the spectral changes are at a maximum.

Even at temperatures above 50 °C, the reactions are slow, requiring several hours to reach completion. In consequence, not all the tabulated kinetic data are quoted for duplicate experiments. Where duplicate experiments were carried out, the results were reproducible. In all experiments the concentration of the nitrogenous base was in great excess over that of the reagent complex, and so its concentration may be assumed to remain constant over the course of a reaction.

When hexakis-methylisonitriloiron(II) reacts with excess hydrazine in aqueous solution, the formation of the tetrakis-methylisonitrilodicarbenoiron(II) product obeys pseudo-first order kinetics. Kinetic data for this reaction are quoted in Table I. Similar kinetic behaviour is also observed for attack by methylhydrazine — Table II.

Within experimental error, the observed rate constant is independent of ionic strength when no acid is added to the reaction solution and shows a first order dependance on the concentration of added hydrazine. When acid is added, at a constant ionic strength, a variation in the observed rate constant occurs. Equation (i) satisfactorily describes this variation.

$$k_{obs} = \{K_1 k_2 [H^+] + k_3\} [N_2H_4] \tag{i}$$

It is reasonable to assign K_1 to the equilibrium (iii). At 20 °C the constant K_1 has a value [12, 13] of 1.58 $\times 10^8 \ M^{-1}$. If the magnitude of K_1 is similar at our working temperatures then the concentration of $N_2H_5^+$ is approximately twice that of the added sulphuric acid. Thus we may estimate k_2 to be approximately 3.4 $\times 10^{-2} M^{-1} \ s^{-1}$, at 69.0 °C and an ionic strength of 1.55 $\times 10^{-2} M$. The rate constant k_3 for the reaction with N_2H_4 is smaller, being 9.5 $\times 10^{-3} \ M^{-1} \ s^{-1}$ at the same temperature. In the absence of added acid, the major term in equation (i) is the k_3 term. Hence, we deduce that the activation data for this term are $\Delta H_3^{\ddagger} = (59 \pm 4.5) \ kJ \ mol^{-1}$ and $\Delta S_3^{\ddagger} = (-42 \pm 9) \ J \ K^{-1} \ mol^{-1}$.

Table I contains one further source of information. Variation of the hydrazine concentration causes

TABLE I. Kinetic Data for the Reaction between $1.00 \times 10^{-4} M$ [Fe(CNCH$_3$)$_6$]$^{2+}$ and N$_2$H$_4$ in Aqueous Solution. The formation of [Fe(CNCH$_3$)$_4$(C$_4$H$_{10}$N$_4$)]$^{2+}$ was followed at 250 nm.

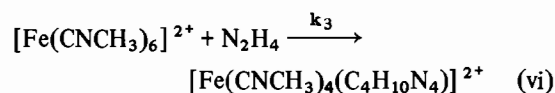| 10^2[N$_2$H$_4$]/M	Temp/°C	10^3[K$_2$SO$_4$]/M	10^3[H$_2$SO$_4$]/M	$10^4 k_{obs}$/s^{-1}	D$_\infty$
2.06	69.0	0	0	2.00	0.890
4.12	69.0	0	0	3.83	0.779
6.18	69.0	0	0	6.00	0.680
8.24	69.0	0	0	7.67	0.610
2.50	59.0	0	0	1.00	0.860
5.00	59.0	0	0	2.43	0.730
7.50	59.0	0	0	3.83	0.625
10.00	59.0	0	0	4.83	0.560
5.00	48.0	0	0	0.84	0.733
10.00	48.0	0	0	1.70	0.562
4.12	64.0	1.72	0	2.77	0.494
4.12	64.0	3.44	0	2.90	0.586
4.12	64.0	5.16	0	2.83	0.598
4.12	64.0	6.88	0	2.87	0.612
5.00	69.0	4.35	0.85	5.70	0.910
5.00	69.0	1.30	3.90	7.12	0.884
5.00	69.0	0.70	4.50	7.45	0.825
5.00	69.0	0	5.20	7.80	0.780

TABLE II. Kinetic Data for the Reaction between $1.36 \times 10^{-4} M$ [Fe(CNCH$_3$)$_6$]$^{2+}$ and CH$_3$N$_2$H$_3$ in Aqueous Solution. The formation of [Fe(CNCH$_3$)$_4$(C$_5$H$_{12}$N$_4$)]$^{2+}$ was followed at 250 nm.

10^2[CH$_3$NHNH$_2$]/M	Temp/°C	$10^4 k_{obs}$/s^{-1}	D$_\infty$
1.45	69.0	0.335	1.495
4.34	69.0	1.05	1.320
7.96	69.0	1.84	1.100
10.10	69.0	2.22	0.967
4.34	51.0	0.602	1.320
4.34	55.0	0.677	1.323
4.34	61.0	1.01	1.320

the final optical density reading, D$_\infty$, to change according to the relationship

$$(D_\infty)_{maximum}/(D_\infty)_{obs} = 1 + K_4[N_2H_4] \qquad (ii)$$

We interpret this in terms of reaction (vii) of the following scheme; a reaction in which the hydrazine acts as a base causing deprotonation of the dicarbene product whose absorption spectrum is being followed. There is also evidence that this product can be protonated when acid is added to the reaction solution.

$$N_2H_4 + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} N_2H_5^+ \qquad (iii)$$

$$[Fe(CNCH_3)_6]^{2+} + N_2H_5^+ \xrightarrow{k_2}$$

$$[Fe(CNCH_3)_4(C_4H_{11}N_4)]^{3+} \qquad (iv)$$

$$[Fe(CNCH_3)_4(C_4H_{11}N_4)]^{3+} \xrightarrow{fast}$$

$$[Fe(CNCH_3)_4(C_4H_{10}N_4)]^{2+} + H^+ \qquad (v)$$

$$[Fe(CNCH_3)_6]^{2+} + N_2H_4 \xrightarrow{k_3}$$

$$[Fe(CNCH_3)_4(C_4H_{10}N_4)]^{2+} \qquad (vi)$$

$$[Fe(CNCH_3)_4(C_4H_{10}N_4)]^{2+} + N_2H_4 \overset{K_4}{\rightleftharpoons}$$

$$[Fe(CNCH_3)_4(C_4H_9N_4)]^+ + N_2H_5^+ \qquad (vii)$$
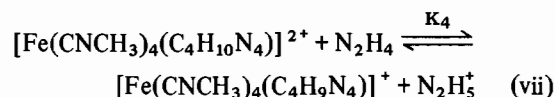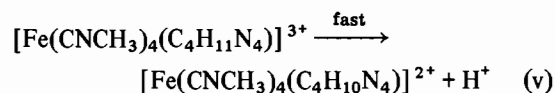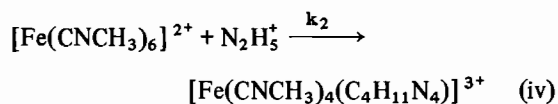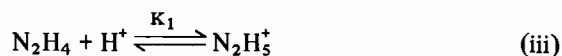
Since the formation of the complex containing the dicarbene involves the formation of a five membered chelate ring, it is reasonable to assume that k_2 and k_3 represent the rates of formation of monodentate carbene complexes which then undergo rapid ring closure to give the observed product: exactly as ring closure is rapid in complex formation in aqueous solution [14].

In Table II, the kinetic data obtained for the reaction with methylhydrazine are quoted. The pattern of behaviour is similar to that discussed above although the activation parameters differ for the two nucleophiles. Thus $\Delta H_3^{\ddagger}$(CH$_3$NHNH$_2$) = (40.3 ± 5) kJ mol^{-1} and $\Delta S_3^{\ddagger}$(CH$_3$NHNH$_2$) = (−123 ± 14) J K^{-1} mol^{-1}, while k_3 = 2.3 × 10$^{-3} M^{-1}$ s^{-1} at 69.0 °C. A comparison of these data with those for attack by hydrazine suggests that there is a marked change in solvation on going from reagents to transition state in the two cases, more solvent molecules becoming involved in the formation of the transition state for the methylhydrazine case than for hydrazine.

Surprisingly, when we turned to methylamine as nucleophile, we found a complete change in the kinetic profile of the reaction. Again we had prepared solutions of the product to identify the best wavelength for study. Subsequently, we were surprised to find that, for a reaction solution, the optical density measured at this wavelength, 240 nm, rose to a maximum and then declined to a lower final value. The final value, D_∞, varies with the concentration of the methylamine in the solution.

Although we were able to find one plausible mechanistic scheme which, in computation, fitted the data for individual kinetic runs, we did not obtain satisfactory reproducibility for the constants obtained from different runs. Therefore we cannot state, with certainty, the mechanism of the reaction involving methylamine. The only scheme with which we obtained reasonable data fitting (with excess methylamine present) can be represented as

$$ X \xrightarrow{k_5} Y \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} Z \qquad \text{(viii)} $$

with the concentration of Y being monitored. The equation

$$ \frac{[Y]}{[X_0]} = $$

$$ \frac{k_{-6}(k_6 + k_{-6} - k_5) + (k_5 - k_{-6})(k_6 + k_{-6})e^{-k_5 t} -}{(k_6 + k_{-6})(k_6 + k_6 - k_{-5})} $$

$$ \frac{k_5 k_6 e^{-(k_6 + k_6)t}}{} \qquad \text{(ix)} $$

would then describe the reaction profile.

While studying carbene formation from rhodium-(III) isonitrile complexes and primary amines, Green and co-workers [15] observed the formation of a monocarbene which was converted to a chelating dicarbene in the presence of neat amine. We believe that we are observing a similar phenomenon here. That is, during our original preparation we obtained the known dicarbene complex: but when dilute aqueous solutions were prepared for spectral investi-

gation the solute reverted to the monocarbene form, which has a greater extinction coefficient at 240 nm than does the dicarbene. Therefore, experiments which follow carbene formation at this wavelength follow the formation of a monocarbene (equivalent to Y in equation viii) and its subsequent equilibration with the complex containing a four membered chelating dicarbene ring (Z of equation viii).

Although the reactions described here have been examined in a different solvent from those already reported for the formation of carbenes on metal ions exhibiting square planar geometry [10, 11], some comparison is possible. The formation of these dicarbenes on Fe(II) seems to involve a slow first step followed by a more rapid ring closure. If the chelate ring formed is a five membered ring then the formation of the first C–N bond is rate determining, but much slower than the equivalent step for Pt(II). These relative rates probably reflect the more crowded co-ordination sphere around Fe(II). While it is more difficult to penetrate and modify this sphere to produce a monocarbene ligand, this same crowding will make ring closure more likely. There is no possible orientation of a monocarbene derived from hydrazine which will not leave the free N close to another isonitrile ligand, essentially a further manifestation of the chelate effect. Attack on a co-ordinated isonitrile ligand by methylamine will not offer such a stable ring since it must be four- rather than five-membered, hence the equlibration between the two isomeric carbene products.

Experimental

Reported methods [6] were followed for the preparation of $[Fe(CNCH_3)_6] [HSO_4]_2$, $[(CH_3NC)_4Fe(C_4H_{10}N_4)] [PF_6]_2$, $[(CH_3NC)_4Fe(C_5H_{12}N_4)] [PF_6]_2$ and $[(CH_3NC)_4Fe(C_5H_{11}N_3)] [PF_6]_2$. In all cases the physical properties and spectra were in agreement with those already reported [5, 6, 16–18], while analytical data were consistent with those expected, see Table III.

All ultra-violet spectra and kinetic data were obtained using a Pye Unicam SP1800 spectrophotometer.

TABLE III. Analytical Data for Products.

Compound	Expected				Found			
	%C	%H	%F	%N	%C	%H	%F	%N
$[Fe(CNCH_3)_6] [HSO_4]_2$	28.1	4.1	–	16.3	28.5	4.2	–	16.5
$[Fe(CNCH_3)_6] [PF_6]_2$	24.3	3.1	38.5	14.2	24.4	3.1	36.7	14.2
$[(CH_3NC)_4Fe(C_4H_{10}N_4)] [PF_6]_2$	23.1	3.6	36.6	18.0	23.8	3.5	35.7	18.0
$[(CH_3NC)_4Fe(C_5H_{12}N_4)] [PF_6]_2$	24.5	3.8	–	17.6	24.6	4.0	–	17.3
$[(CH_3NC)_4Fe(C_5H_{11}N_3)] [PF_6]_2$	25.1	3.7	39.8	15.7	25.3	3.6	37.4	16.1

Acknowledgment

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