Blue Transient Complex Formation in the Electron–transfer Reaction between Iron(III) and a Reduced Nicotinamide–Adenine Dinucleotide Analogue without an Amide Group

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A blue transient complex with a stoicheiometry $[Fe(C_{13}H_{10}NMe)]^{3+}$ is formed very rapidly in the electron transfer from 9,10-dihydro-10-methylacridine ($C_{13}H_{10}NMe$) to Fe^{3+} in acetonitrile at 298 K. The disappearance of the absorption band ($\lambda_{max.}$ 640 nm) due to $[Fe(C_{13}H_{10}NMe)]^{3+}$ obeys pseudo-first-order kinetics, and is accompanied by the appearance of an absorption band ($\lambda_{max.}$ 358 nm) due to the oxidized product, 10-methylacridinium ion ($C_{13}H_9NMe^+$).

The biological importance of NADH (reduced nicotinamide–adenine dinucleotide) as an electron source has stimulated extensive studies on electron-transfer reactions from NADH and its analogues to various one-electron oxidants.[1] Electron-transfer reactions of NADH analogues reported so far involve co-ordinately saturated iron(III) complexes such as $[Fe(CN)_6]^{3-}$,[2,3] $[Fe(C_5H_5)_2]^+$,[4] and $[Fe(L-L)_3]^{3+}$ (L–L = 2,2′-bipyridine or 1,10-phenanthroline),[5] and thus proceed *via* an outer-sphere pathway with no appreciable interaction between the NADH analogues and oxidants which are inert towards substitution. Such an outer-sphere electron-transfer pathway has been well established also for photo-induced electron-transfer reactions of NADH analogues.[1,6] On the other hand, transient blue complexes ($\lambda_{max.}$ 540 nm) are formed with stoicheiometries $[Fe(NADH)]^{3+}$ and $[Fe(NADH)_2]^{3+}$ in electron-transfer reactions from NADH to iron(III) perchlorate.[7] Based on resonance-Raman studies,[8] these have been suggested to be π complexes formed between iron(III) and the nicotinamide ring. However, the role of the amide group remains unclear. In addition, no transient iron(III) complexes of NADH analogues have so far been reported, although stable high-spin iron(III) porphyrin complexes are known to be formed with various NADH analogues.[9]

We report herein that a blue transient iron(III) complex is formed with a NADH analogue, 9,10-dihydro-10-methylacridine ($C_{13}H_{10}NMe$), which has no amide group. The stoicheiometry and the kinetics of the formation and decay of this complex have been examined using a stopped-flow technique, and its role in the electron-transfer reaction from $C_{13}H_{10}NMe$ to Fe^{3+} is discussed.

Experimental

9,10-Dihydro-10-methylacridine ($C_{13}H_{10}NMe$) was prepared from 10-methylacridinium iodide ($C_{13}H_9NMe^+I^-$) by reduction with $NaBH_4$ in methanol, and purified by recrystallization from ethanol.[10] The preparation and purification of 1-benzyl-1,4-dihydronicotinamide (1-benzyl-1,4-dihydropyridine-3-carboxamide) were as described elsewhere.[11] Iron(III) perchlorate was obtained commercially. Acetonitrile was purified by the standard procedure.[12]

Kinetic measurements were carried out using a Union RA-103 stopped-flow spectrophotometer under deaerated conditions at 298 K. Transient spectra were obtained by measuring the change in absorbance at various wavelengths. Rates of electron transfer from $C_{13}H_{10}NMe$ to Fe^{3+} were monitored by the increase in absorbance at $\lambda_{max.}$ 358 nm of $C_{13}H_9NMe^+$ or by the decrease in absorbance at $\lambda_{max.}$ 640 nm of $[Fe(C_{13}H_{10}NMe)]^{3+}$ at various initial concentrations of $C_{13}H_{10}NMe$ and Fe^{3+} under pseudo-first-order conditions. Pseudo-first-order rate constants were determined by least-squares curve fitting using a Union System 77 microcomputer. The stoicheiometry of the reaction was determined from a plot of the concentration of $C_{13}H_9NMe^+$ formed *vs.* the ratio of the initial concentrations of $C_{13}H_{10}NMe$ to Fe^{3+}.

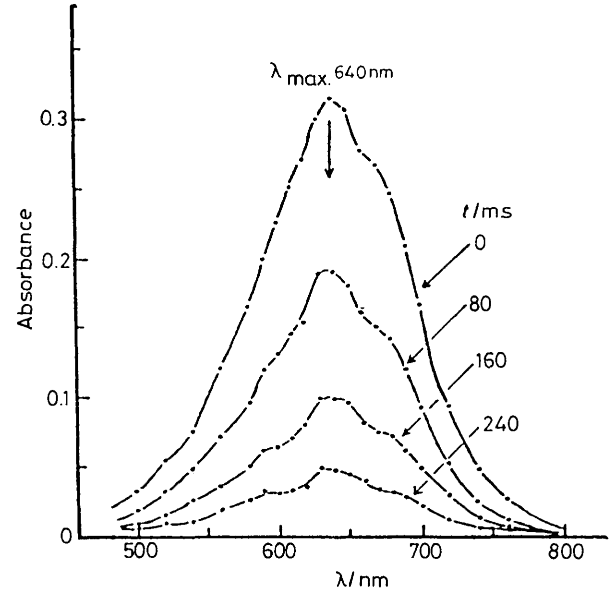


Figure 1. Transient absorption spectra observed in the electron-transfer reaction from $C_{13}H_{10}NMe$ to $Fe(ClO_4)_3$ in acetonitrile at 298 K

Results and Discussion

Mixing an acetonitrile solution of $Fe(ClO_4)_3$ with $C_{13}H_{10}NMe$ in the stopped-flow spectrophotometer results in the instant appearance of a new absorption band at $\lambda_{max.}$ 640 nm (Figure 1),

Table. Pseudo-first-order rate constants $k_{obs.}$ for the decay of $[Fe(C_{13}H_{10}NMe)]^{3+}$ and the formation of $C_{13}H_9NMe^+$ in acetonitrile at 298 K; $\lambda_{max.}$ = 640 nm in each case

$[Fe^{3+}]$/mol dm^{-3}	$[C_{13}H_{10}NMe]$/mol dm^{-3}	$k_{obs.}$*/ s^{-1}
5.0×10^{-3}	5.0×10^{-4}	8.5
2.5×10^{-3}	2.5×10^{-4}	5.2
1.4×10^{-4}	5.0×10^{-3}	8.7 (8.6)
5.4×10^{-4}	2.5×10^{-5}	1.6
2.7×10^{-4}	2.5×10^{-5}	0.90

* Determined from the formation of $C_{13}H_9NMe^+$. The value in parentheses was determined from the decay of $[Fe(C_{13}H_{10}NMe)]^{3+}$. The experimental errors are ±10%.

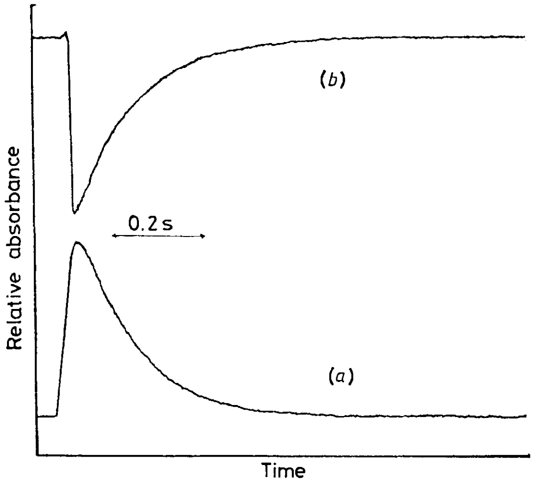


Figure 2. Decay (*a*) and rise (*b*) of the absorbance at 640 and 358 nm respectively in the electron-transfer reaction from $C_{13}H_{10}NMe$ (5.0×10^{-3} mol dm^{-3}) to Fe^{3+} (1.4×10^{-4} mol dm^{-3}) in acetonitrile at 298 K

followed by its decay. The new band may be ascribed to the formation of a complex between Fe^{3+} and $C_{13}H_{10}NMe$. The transient absorption spectra were measured at various ratios of $[Fe^{3+}]$ to $[C_{13}H_{10}NMe]$. There is no change in the shape, only in the intensity of the spectra, as shown in the Table. The same absorbance was obtained when the ratio of $[Fe^{3+}]$ to $[C_{13}H_{10}NMe]$ was reversed. Thus, the stoicheiometry of the complex between Fe^{3+} and $C_{13}H_{10}NMe$ must be 1:1, equation (1). The absorption coefficient of $\lambda_{max.}$ 640 nm was determined

$$Fe^{3+} + C_{13}H_{10}NMe \overset{K}{\rightleftharpoons} [Fe(C_{13}H_{10}NMe)]^{3+} \quad (1)$$

as 1.1×10^4 dm^3 mol^{-1} cm^{-1}. The decrease in the absorbance at $\lambda_{max.}$ 640 nm due to $[Fe(C_{13}H_{10}NMe)]^{3+}$ coincides with an increase in absorbance at $\lambda_{max.}$ 358 nm due to the oxidized product, 10-methylacridinium ion ($C_{13}H_9NMe^+$) as shown in Figure 2. The stoicheiometry of the electron-transfer reaction was determined as described in the Experimental section and given by equation (2). Replacement of $C_{13}H_{10}NMe$ by another NADH analogue, 1-benzyl-1,4-dihydronicotinamide also results in a facile oxidation to 1-benzyl-3-carbamoylpyridinium. In this case, however, the reaction is too fast to monitor by the stopped-flow technique.

The decay of $[Fe(C_{13}H_{10}NMe)]^{3+}$ as well as the formation of $C_{13}H_9NMe^+$ obeys pseudo-first-order kinetics. The observed rate constant $k_{obs.}$ for the decay of $[Fe(C_{13}H_{10}NMe)]^{3+}$ agrees with that for the formation of $C_{13}H_9NMe^+$ (Table). This agreement does not, by itself, prove that the complex lies along the reaction pathway of the electron-transfer reaction from $C_{13}H_{10}NMe$ to Fe^{3+} to yield $C_{13}H_9NMe^+$. The complex formation may represent an unrelated side reaction.[13] The difference lies in whether the rate-limiting step is a reaction (k_i) of the complex [equation (3)], or a bimolecular reaction (k_b) (4) in which the complex is an innocent bystander. In both cases,

$$Fe^{3+} + C_{13}H_{10}NMe \overset{K}{\rightleftharpoons} [Fe(C_{13}H_{10}NMe)]^{3+} \xrightarrow{k_i} Fe^{2+} + C_{13}H_{10}NMe^{\bullet +} \quad (3)$$

$$[Fe(C_{13}H_{10}NMe)]^{3+} \overset{K}{\rightleftharpoons} Fe^{3+} + C_{13}H_{10}NMe \xrightarrow{k_b} Fe^{2+} + C_{13}H_{10}NMe^{\bullet +} \quad (4)$$

$C_{13}H_{10}NMe^{\bullet +}$ may be deprotonated by the solvent which contains water to give $C_{13}H_9NMe^{\bullet}$ [equation (5)] and subsequent facile electron transfer from $C_{13}H_9NMe^{\bullet}$ to Fe^{3+} occurs to yield $C_{13}H_9NMe^+$ and Fe^{2+} [equation (6)]. The

$$C_{13}H_{10}NMe^{\bullet +} \xrightarrow{\text{fast}} C_{13}H_9NMe^{\bullet} + H^+ \quad (5)$$

$$Fe^{3+} + C_{13}H_9NMe^{\bullet} \xrightarrow{\text{fast}} Fe^{2+} + C_{13}H_9NMe^+ \quad (6)$$

second electron transfer cannot be rate determining, since the oxidation potential of $C_{13}H_9NMe^{\bullet}$ (−0.43 V *vs.* s.c.e.)[6] is much more negative than that of $C_{13}H_{10}NMe$ (0.80 V *vs.* s.c.e.)[6] and thereby the second electron transfer [equation (6)] is energetically much more favourable than the first [equation (3) or (4)].

If $[Fe(C_{13}H_{10}NMe)]^{3+}$ participates in the equilibrium (4) the observed pseudo-first-order rate constant $k_{obs.}$ for the decay of $[Fe(C_{13}H_{10}NMe)]^{3+}$ as well as the formation of $C_{13}H_9NMe^+$ in the presence of a large excess of Fe^{3+} is given by equation (7), which can be rewritten as (8). Alternatively, if $[Fe(C_{13}H_{10}NMe)]^{3+}$ lies along the reaction pathway (3), $k_{obs.}$ is given by equation (9), which can be rewritten as (10). Equations (7) and (8) are kinetically indistinguishable from (9)

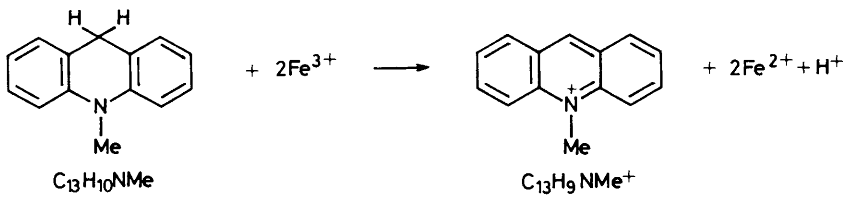
$$k_{obs.} = k_b[Fe^{3+}]/(1 + K[Fe^{3+}]) \quad (7)$$

$$k_{obs.}^{-1} = k_b^{-1}(K + [Fe^{3+}]^{-1}) \quad (8)$$

$$k_{obs.} = k_iK[Fe^{3+}]/(1 + K[Fe^{3+}]) \quad (9)$$

$$k_{obs.}^{-1} = k_i^{-1}(1 + K^{-1}[Fe^{3+}]^{-1}) \quad (10)$$

and (10), and both cases predict a linear correlation between $k_{obs.}^{-1}$ and $[Fe^{3+}]^{-1}$. The $k_{obs.}$ values at various concentrations of



(2)

$C_{13}H_{10}NMe$ $C_{13}H_9NMe^+$

Fe^{3+} are given in the Table, and a plot of $k_{obs.}^{-1}$ *vs.* $[Fe^{3+}]^{-1}$ is linear. When equations (8) and (10) are applied to the linear correlation the K value obtained is 2.7×10^2 dm^3 mol^{-1} from the ratio of the intercept to slope, and k_i and k_b are 13 s^{-1} and 3.5×10^3 dm^3 mol^{-1} s^{-1}, respectively.

The blue transient complex formed between Fe^{3+} and $C_{13}H_{10}NMe$ which contains no amide group may be a π complex between iron(III) and the acridine ring as reported for blue iron(III) complexes of NADH, since the acridine ring tertiary nitrogen is known to be a very weak base.[8] As such, an amide group is not required for blue complex formation between Fe^{3+} and a NADH analogue. The absorption maximum of $[Fe(C_{13}H_{10}NMe)]^{3+}$ ($\lambda_{max.}$ 640 nm) is red shifted compared with that of $[Fe(NADH)]^{3+}$ ($\lambda_{max.}$ 540 nm)[7] probably because of the greater delocalization in the acridine π orbitals than those of the nicotinamide ring. The π complex may be stabilized by ligand-to-metal charge-transfer (l.m.c.t.) interaction. The degree of charge transfer may be close to 100%, since the absorption maxima of $[Fe(C_{13}H_{10}NMe)]^{3+}$ ($\lambda_{max.}$ 640 nm) and $[Fe(NADH)]^{3+}$ ($\lambda_{max.}$ 540 nm) are the same as those of the free radical cations, $C_{13}H_{10}NMe^{\bullet+}$ ($\lambda_{max.}$ 640 nm)[14] and $NADH^{\bullet+}$ ($\lambda_{max.}$ 540 nm).[15]

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